

**Supporting Information for**  
**Amino Induced High-Loading Atomically Dispersed Co sites**  
**on N-doped Hollow Carbon for Efficient CO<sub>2</sub>**  
**Transformation**

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## S1. Materials and Instrumentation

All chemicals are commercially available and used without further purification: Zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , Sinopharm Chemical Reagent Co.,Ltd., AR,  $\geq 99\%$ ), 2-methylimidazole (MeIM, Shanghai Acme Biochemical Co.Ltd, 95%), Cobalt (II) binitrate hexahydrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , Shanghai Acme Biochemical Co.Ltd, AR, 99%), Dopamine hydrochloride (aladdin, 98%), Tetrabutylammonium bromide (TBAB, aladdin, AR, 99%), Styrene oxide (Shanghai Acme Biochemical Co.Ltd, 98%), Ethanol (Sinopharm Chemical Reagent Co.,Ltd., AR,  $\geq 99.7\%$ ), Absolute methanol (Sinopharm Chemical Reagent Co.,Ltd., AR,  $\geq 99.5\%$ ), Ethyl acetate (Sinopharm Chemical Reagent Co.,Ltd., AR, 99.5%), N,N-Dimethylformamide (DMF, Sinopharm Chemical Reagent Co.,Ltd., AR,  $\geq 99.5\%$ ), Ammonia solution (Sinopharm Chemical Reagent Co.,Ltd., AR, 25.0%~28.0%), Deionized water with 18.25  $\text{M}\Omega \cdot \text{cm}$  resistance from Millipore system.

Powder X-ray diffraction (PXRD) patterns were collected on a Germany Bruker D8 Advance X-ray diffractometer equipped with graphitic monochromatized  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Field-emission scanning electron microscopy (FE-SEM) was carried out with a Hitachi 8100 field emission scanning electron microanalyzer at an acceleration voltage of 5 kV). The transmission electron microscopy (TEM) observation was acquired on Hitachi HT7700 with an electron acceleration voltage of 200 kV. The spherical aberration-corrected high-angle annular dark-field scanning

transmission electron microscopy (HAADF-STEM) images were acquired on a Japan JEM-ARM200F instrument at 200 keV. The Raman spectrogram of the samples were recorded on a Britain Renishaw inVia equipped with laser whose excitaton wavelength is 532 nm. The surface area of the samples was estimated by Brunauer-Emmett-Teller (BET) method and the pore size distribution was obtained from the DFT method in the USA Micromeritics ASAP 2460 software package based on the N<sub>2</sub> sorption at 77 K. X-ray photoelectron spectroscopy (XPS) measurements were conducted by utilizing a thermo ESCALAB 250 high-performance electron spectrometer using monochromatized Al K $\alpha$  ( $h\nu = 1486.6$  eV) as the excitation source. The CO<sub>2</sub> adsorption isotherm of samples was tested by the USA Micromeritics 3Flex gas adsorbent equipped with Dewar of low-temperature thermoelectric refrigeration and the CO<sub>2</sub> isosteric heat of adsorption for sample surface coverage (from zero to saturation) was calculated based on MicroActive software system. The catalytic reaction products were analyzed and identified by Japan Shimadzu gas chromatography-mass spectrometry (GC-MS-QP2020). The content of Co atoms in the catalyst was quantified by an Optima 7300 DV inductively coupled plasma atomic emission spectrometer (ICP-AES).

### **XAFS measurements**

The X-ray absorption fine structure (XAFS) spectra data (Co K-edge) were recorded at 1W1B station in Beijing Synchrotron Radiation Facility (BSRF, electron storage ring operated at 2.5 GeV with a maxium current of 250 Ma and labxafs, Rapidxafs 1M). The data were collected in fluorescence excitation mode using a Lytle detector. All solid samples were pelletized as disks of 13 mm diameter with 1 mm thickness using

graphite powder as a binder and measured at room temperature.

## **S2. Preparation of Samples.**

**Preparation of ZIF-8:** Firstly, 3.72 g zinc nitrate hexahydrate and 4.11 g 2-methylimidazole were ultrasonically dissolved in 100 mL anhydrous methanol for 10 min, respectively. Then, the solution containing 2-methylimidazole was added into the zinc nitrate solution to form a mixed solution. Subsequently, the mixed solution was sonicated until it appeared precipitated, and stood for more than 12 h at room temperature. Finally, the precipitate was collected by centrifugation, washed three times with anhydrous methanol and dried in a vacuum drying oven at 70 °C for overnight. The dried product was further grinded in a mortar to obtain a white powder, namely ZIF-8.

**Preparation of ZIF-8@Co-Dopamine:** At first, 300 mg of the synthesized ZIF-8 was dissolved in a mixed solution composed of 100 ml deionized water, 40 ml ethanol and 2 ml ammonia solution to form solution A; 24 mg cobalt nitrate hexahydrate and 41 mg dopamine (DA) hydrochloride were dissolved in a mixed solvent containing 6 ml deionized water and 4 ml ethanol to form solution B. After solution A and solution B were respectively stirred for 30 minutes at room temperature, then solution A was added into solution B to form another mixed solution C. After solution C was continuously stirred for more than 12 hours at room temperature, the precipitate was collected by centrifugation, washed several times with a mixed solvent of ethanol: deionized water=1:3 and dried in a vacuum drying oven at 70 °C for overnight. The dried product was further grinded in a mortar to obtain a brown-black powder, namely ZIF-8@Co-

Dopamine.

**Preparation of H-Co/ZIF-8:** The synthesis method of H-Co/ZIF-8 is the same as that of ZIF-8@Co-Dopamine, except that no dopamine (DA) hydrochloride is added into solution B and the amount of cobalt nitrate hexahydrate was replaced by 60 mg.

**Preparation of Co/ZIF-8:** The synthesis method of Co/ZIF-8 is the same as that of ZIF-8@Co-Dopamine, except that no dopamine (DA) hydrochloride is added into solution B.

**Preparation of H-Co<sub>SAs</sub>/NHC:** Typically, 400 mg of the obtained ZIF-8@Co-Dopamine was placed in a porcelain boat and put into a flow-through tube furnace. The furnace was heated to 900 °C with heating rate of 5 °C/min under Ar atmosphere with a flow rate of 60 mL/min, and then maintained at 900 °C for 2 h, followed by cooling down to room temperature in Ar atmosphere to give black power. And then washed with deionized water and drying at 70 °C overnight in a vacuum drying oven, the H-Co<sub>SAs</sub>/NHC was obtained.

**Preparation of Co<sub>NPs</sub>/NHC:** Typically, 400 mg of the obtained H-Co/ZIF-8 was placed in a porcelain boat and put into a flow-through tube furnace. The furnace was heated to 900 °C with heating rate of 5 °C/min under Ar atmosphere with a flow rate of 60 mL/min, and then maintained at 900 °C for 2 h, followed by cooling down to room temperature in Ar atmosphere to give Co<sub>NPs</sub>/NHC (Figure S10).

**Preparation of ZIF-8@Dopamine (ZIF-8@DA):** The synthesis method of ZIF-8@DA is the same as that of ZIF-8@Co-DA, except that no cobalt nitrate hexahydrate is added into solution B.

**Preparation of NHC:** The obtained ZIF-8@DA was calcined in a tube furnace to give NHC, the synthesis method and parameters are the same as that of Co<sub>NPs</sub>/NHC.

**Preparation of Co<sub>SAs</sub>/NC:** The obtained Co-ZIF-8 was calcined in a tube furnace, the synthesis method and parameters are the same as that of H-Co<sub>SAs</sub>/NHC.

## Procedure for the Catalytic Cycloaddition Reaction of CO<sub>2</sub> with Epoxides

In general, a mixture of 8 mg catalyst, 0.1 mmol TBAB, 3 mL DMF, 0.22 mmol epoxide was placed into an autoclave. The autoclave was purged with CO<sub>2</sub> for three times to allow pure CO<sub>2</sub> atmosphere for the reaction. The catalytic cycloaddition reaction was carried out under 60 °C provided by the electric furnace of the controller for 2 h at 3 bar pressure. After the reaction, the resultant mixed solution was centrifuged and 2 mL of the supernatant was taken into 2 mL of ethyl acetate, after shaking well, the reaction product was extracted to the upper layer of ethyl acetate, 1 mL of the supernatant ethyl acetate was taken into 3 mL of ethanol. Then, 150 μL sample taken out from the above ethanol with a syringe was detected and quantified by GC-MC.

**Extended Data Table S1** | Structural parameters of H-Co<sub>SAs</sub>/NHC extracted from the EXAFS fitting. ( $S_0^2=0.80$ )

Sample	Scattering		R(Å)	$\sigma^2(10^{-3}\text{Å}^2)$	$\Delta E_0(\text{eV})$
	Co-N	CN			
Sample	Co-N	4.0±0.3	1.93±0.02	5.8±0.6	3.3±0.3

$S_0^2$  is the amplitude reduction factor  $S_0^2=0.8$ ; CN is the coordination number; R is interatomic distance (the bond length between central atoms and surrounding

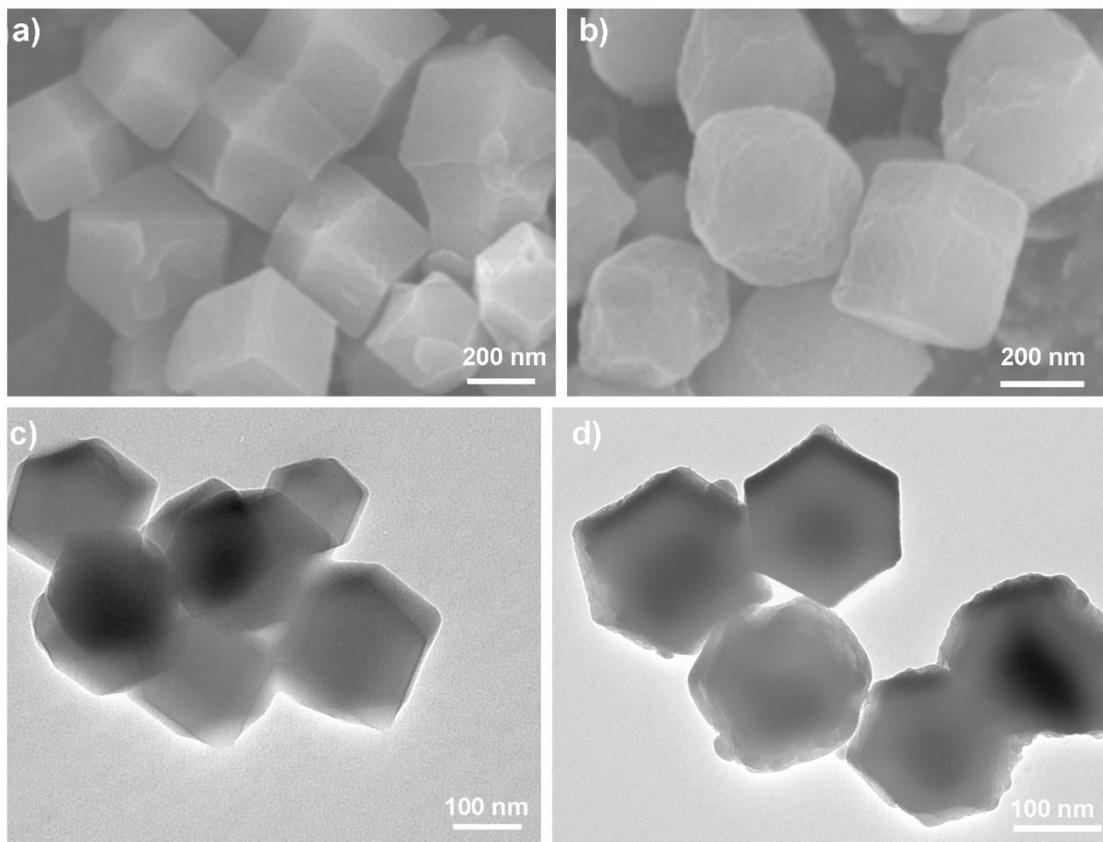
coordination atoms);  $\sigma^2$  is Debye-Waller factor (a measure of thermal and static disorder in absorber-scatterer distances);  $\Delta E_0$  is edge-energy shift (the difference between the zero kinetic energy value of the sample and that of the theoretical model).

R factor is used to value the goodness of the fitting.

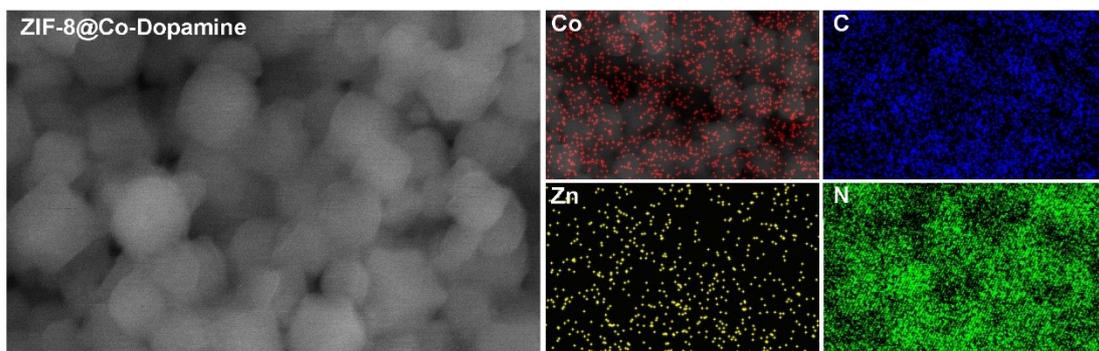
**Table S2.** The list of reported single atom sites with high metal contents.

Entry	Single site	Content	Ref.
1	Co	9.7	This work
2	Co	3.2	This work
3	Co	4	S1
4	Fe	8.9	S2
5	Fe	30	S3

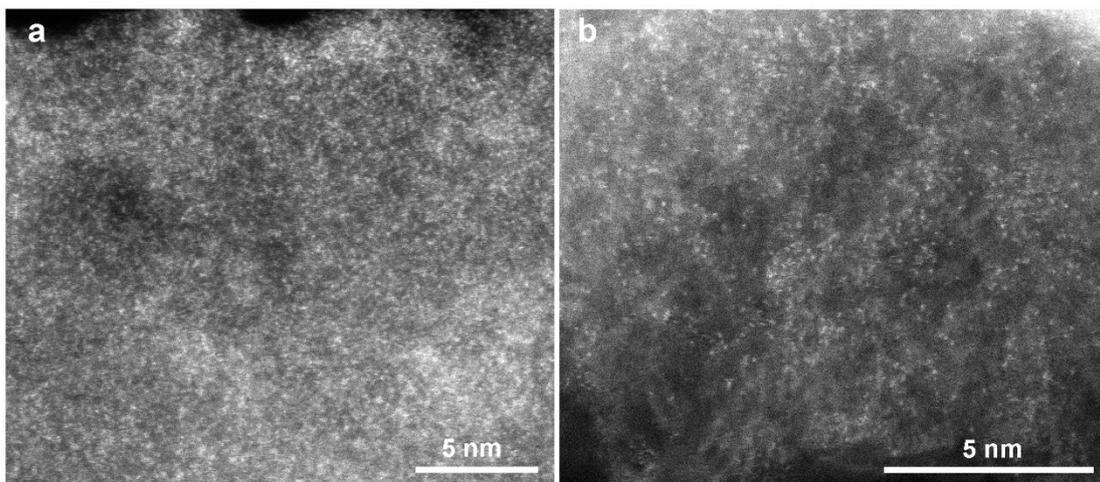
### **S3. Characterization of Samples**



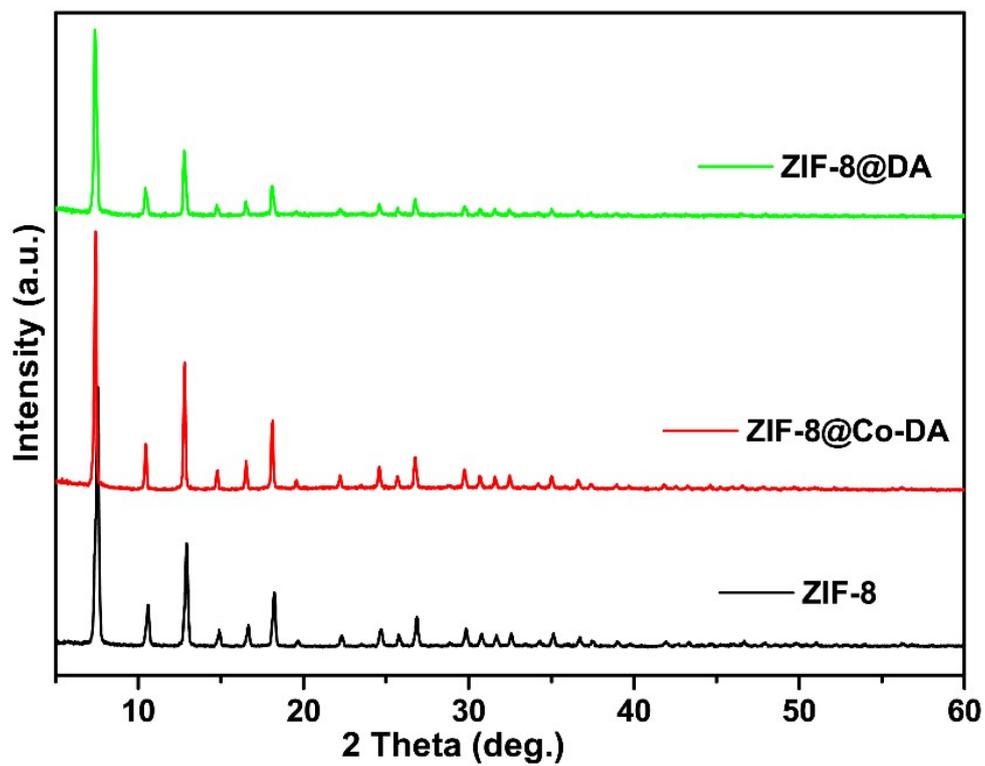
**Fig. S1.** SEM images of a) ZIF-8 and b) ZIF-8@Co-dopamine; c) and d) TEM images of ZIF-8 and ZIF-8@Co-dopamine.



**Fig. S2.** The SEM elements mapping of ZIF-8@Co-Dopamine.



**Fig. S3.** a) The spherical aberration-corrected HAADF-STEM image of the H-Co<sub>SAs</sub>/NHC and b) Co<sub>SAs</sub>/NC.



**Fig. S4.** Powder XRD patterns for ZIF-8, ZIF-8@Co-Dopamine, and ZIF-8@Dopamine.

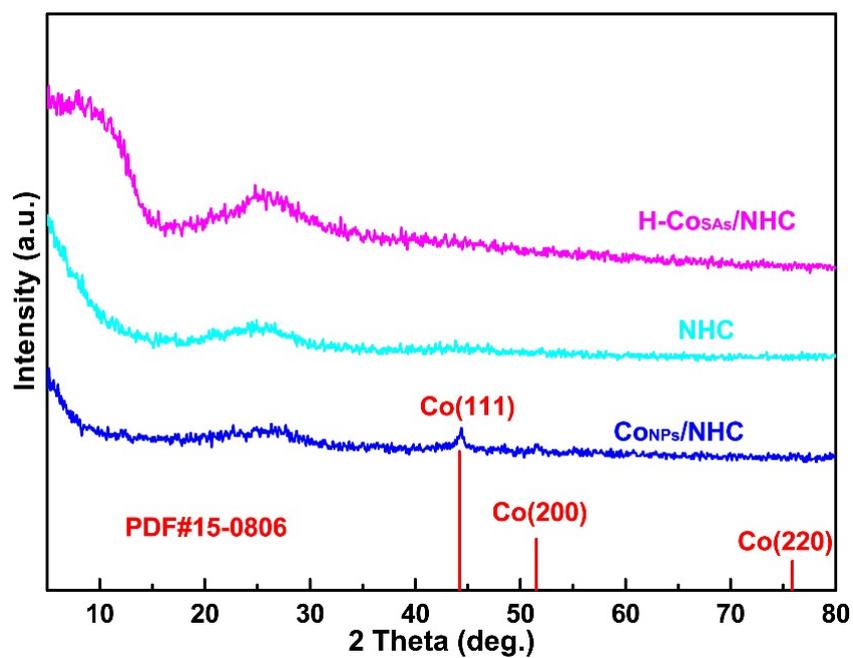


Fig. S5. The Power XRD patterns of the different catalysts:  $\text{Co}_{\text{NPs}}@/\text{NHC}$ , NHC, and  $\text{H-Co}_{\text{SAs}}/\text{NHC}$ .

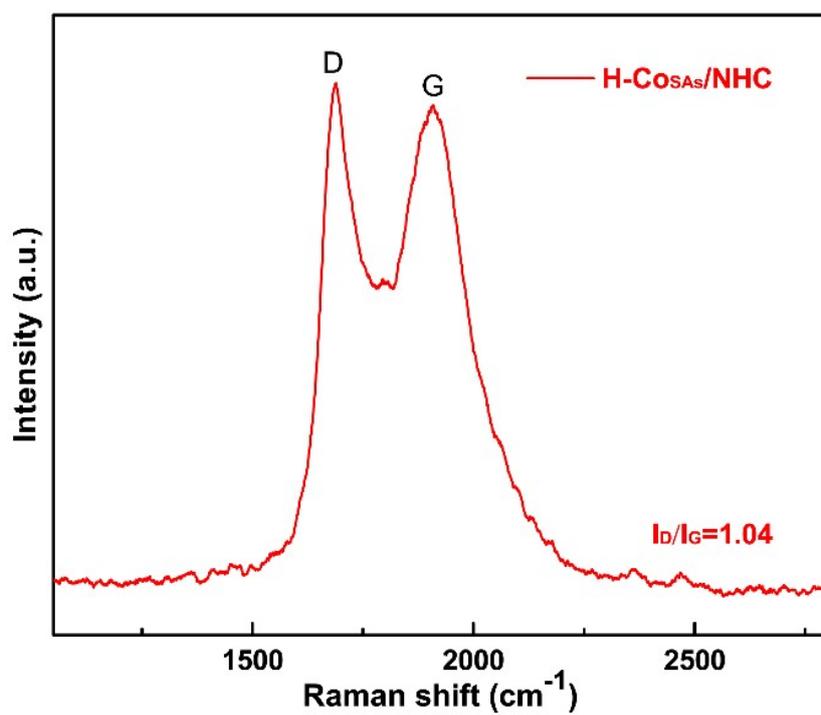
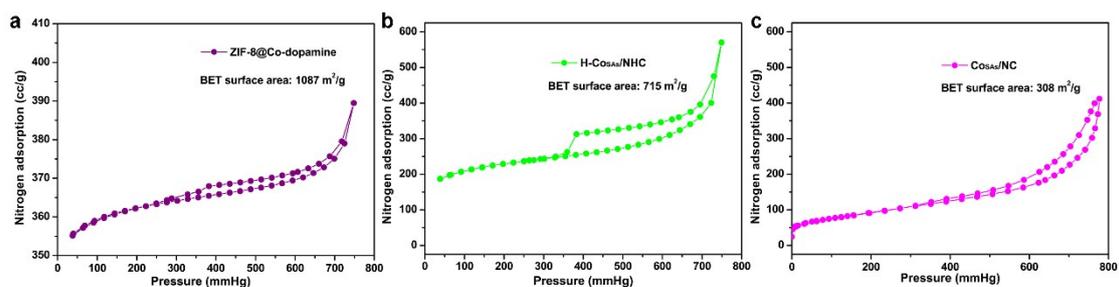
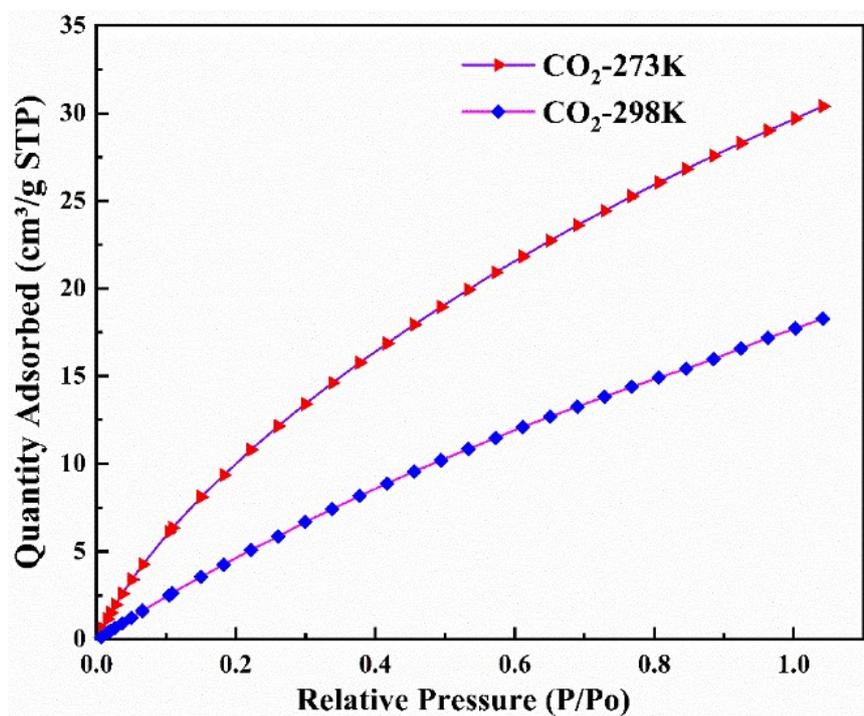


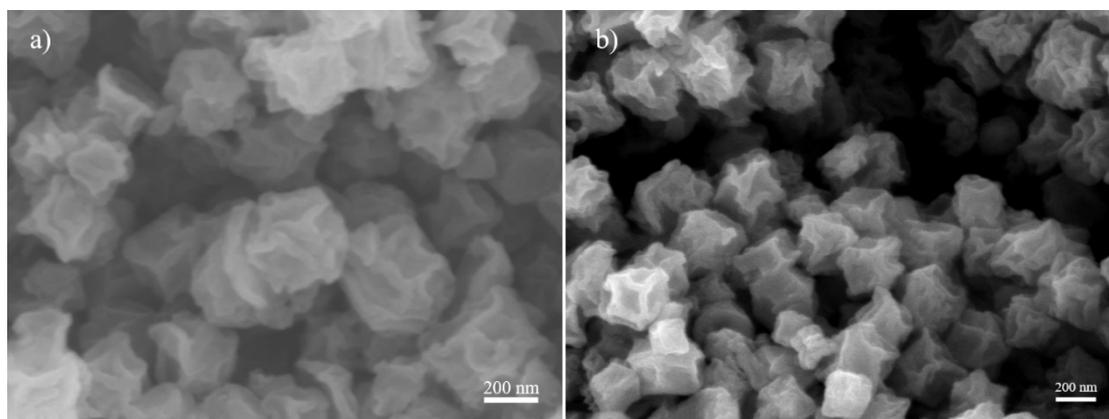
Fig. S6. The Raman spectra of  $\text{H-Co}_{\text{SAs}}/\text{NHC}$  catalyst.



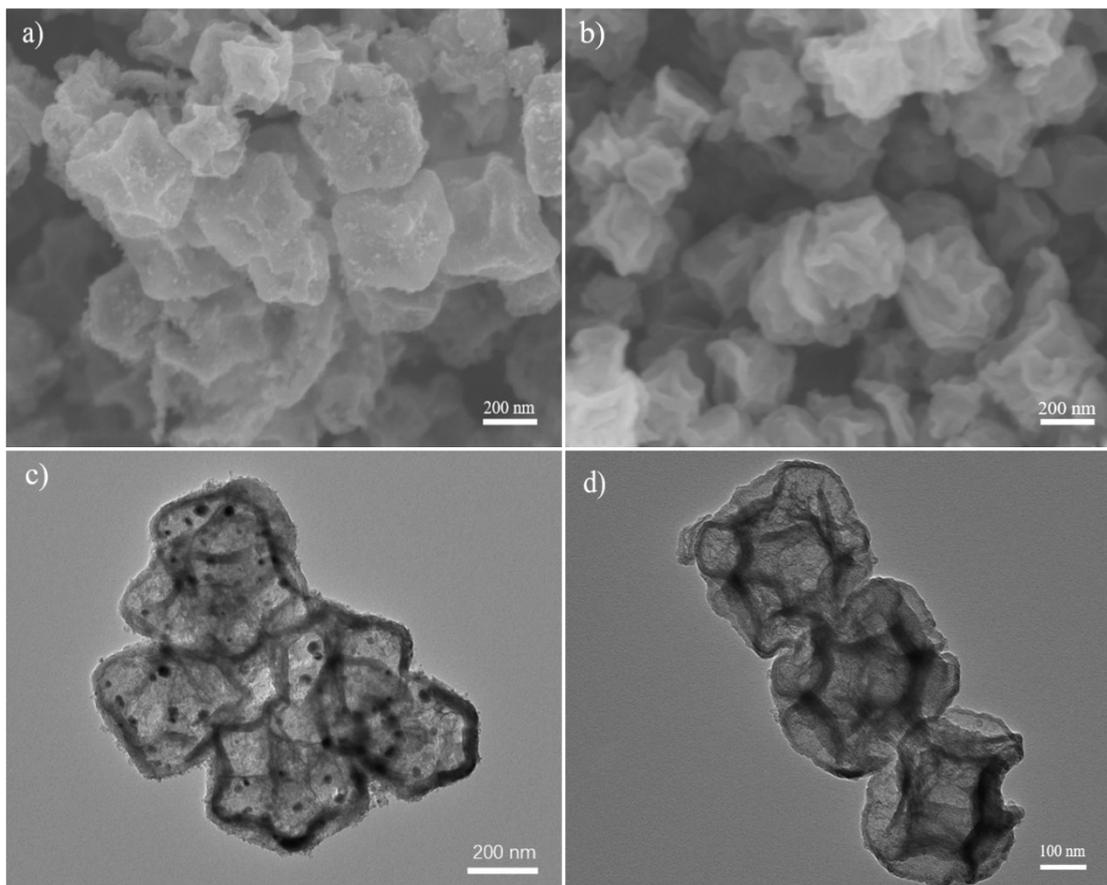
**Fig. S7.** a), b), and c) the  $N_2$  sorption isotherms at 77K of ZIF-8@Co-Dopamine, H- $Co_{SAs}$ /NHC, and  $Co_{SAs}$ /NHC, respectively.



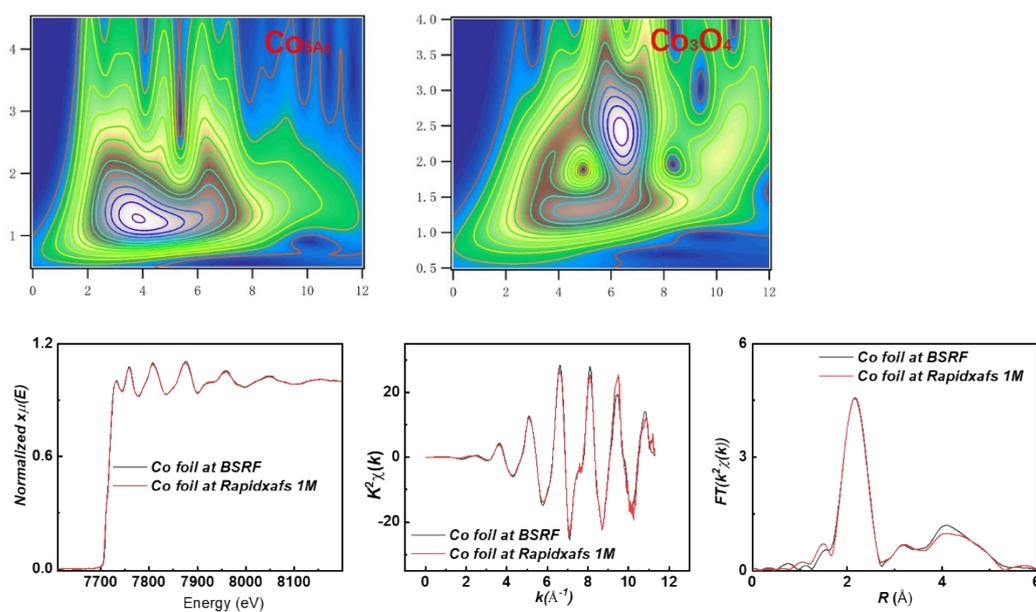
**Fig. S8.**  $CO_2$  sorption isotherms of H- $Co_{SAs}$ /NHC at 273 K and 298 K.



**Fig. S9.** a) and b) are SEM images of the H- $Co_{SAs}$ /NHC before and after the reaction, respectively.



**Fig. S10.** a) and b) the SEM images of  $\text{Co}_{\text{NPs}}/\text{NC}$  and  $\text{H-Co}_{\text{SAs}}/\text{NHC}$ ; c) and d) the TEM images of  $\text{Co}_{\text{NPs}}/\text{NHC}$  and  $\text{H-Co}_{\text{SAs}}/\text{NHC}$ .



**Fig. S11.** WT contour plots of  $\text{Co}_{\text{SAs}}$  (up left); WT contour plots of  $\text{Co}_3\text{O}_4$  (up right); the experimental XAFS curves of Co foil at BSRF and Co foil at Rapidxfas 1M (down).

## References

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