

Figure S1 Optimized structures of H\* adsorbed on (a) Co<sub>4</sub> and (b) Co<sub>2</sub>Fe<sub>2.</sub>



**Figure S2** (a,b) SEM images of S-700, S-800 (c) TEM of S-600 after 10000<sup>th</sup> cycles (d,e) SEM and TEM of Co/graphene (f) TEM image of graphene.



**Figure S3** SEM image of Fe<sub>3</sub>[Co(CN)<sub>6</sub>]<sub>2</sub> precursor.



Figure S4 High resolution transmission electron microscopy (HRTEM) of the S-600



Figure S5 High resolution transmission electron microscopy (HRTEM) of the S-700



Figure S6 High resolution transmission electron microscopy (HRTEM) of the S-800



Figure S7 XRD pattern of Co/graphene sample.



**Figure S8** XPS spectra of S-600, S-700, S-800: (a) wide spectrum; (b) Co 2p spectrum; (c) Fe 2p spectrum; (d) N1s spectrum.



Figure S9 Raman spectra of S-700, S-800



**Figure S10** The thermogravimetry results of Fe<sub>3</sub>[Co(CN)<sub>6</sub>]<sub>2</sub> spheres un der nitrogen atmosphere. The red line is the decomposition curve.



**Figure S11** Nitrogen adsorption-desorption isotherm and the corresponding pore size distribution of S-600, S-700, S-800 materials.



**Figure S12** Optimized structure (a) and charge-density difference (b) of Co4 cluster located above graphitic nitrogen doped graphene. The isosurface value of the color region is  $0.08 \text{ e} \text{ Å}^{-3}$ . The yellow and blue regions refer to increased and decreased charge distributions, respectively.



**Figure S13** (a) Cyclic voltammograms of S-600 within the range of 0.1 to 0.2 V vs RHE with scan rate from 20mV/s to 180mV/s. (b) Variation of double-layer charging currents at 0.15 V vs RHE with potential scan rate.



Figure S14 Time-dependent current density curves (i-t curve) under static overpotentials of 300 mV vs RHE for 11 h.

Samples	C (atom%)	N (atom%)	O (atom%)	Fe (atom%)	Co (atom%)
S-600	65.01	8.22	17.92	4.36	4.48
S-700	79.51	4.54	9.47	3.71	2.71
S-800	83.76	3.08	7.67	3.36	2.14

**Table S1** Chemical compositions of samples prepared at different annealing temperatures by XPS measurement.

Samples	BET surface area	Total pore volume	Pore diameter
S-600	66.2 m <sup>2</sup> g <sup>-1</sup>	$0.22 \text{ cm}^3\text{g}^{-1}$	130.8 Å
S-700	80.9 m <sup>2</sup> g <sup>-1</sup>	$0.22 \text{ cm}^3\text{g}^{-1}$	107.3 Å
S-800	89.2 m <sup>2</sup> g <sup>-1</sup>	0.22 cm <sup>3</sup> g <sup>-1</sup>	99.8 Å

**Table S2** BET surface and Pore characteristic of the obtained S-600, S-700, S-800 materials. Even though the BET surface area of samples will increase with the increasing of annealing temperatures (the similar situation also occurred in other MOFs such as ZIF-8 derived materials in ref 23 of main article), the difference between them is not very big. Besides the S-800 with the largest surface area exhibits the worst catalytic performance, confirming the effect of surface area on activity is negligible in our materials compared with other influencing factors.

Material synthesis:

To obtain S-600,S-700,S-800, the MOF precursor  $Fe_3 [Co(CN)_6]_2$  was directly carbonized under a nitrogen flow under different temperatures (600°C, 700°C, 800°C) with a heating rate of 5 °C min<sup>-1</sup> and kept for 4 h.

The pure graphene used as reference was synthesized with a modified Hummers' method according to the research.<sup>1</sup>

The Co/graphene used as reference was obtained by directly carbonization of Co<sub>3</sub>  $[Co(CN)_6]_2$ . The typical synthetic experiments of Co<sub>3</sub>  $[Co(CN)_6]_2$  were carried out as follows: Solution A: Co (CH<sub>3</sub>COO)<sub>2</sub>·nH2O (0.075 mmol, 18.7 mg) was dissolved in H<sub>2</sub>O (10 mL) under agitated stirring to obtain a transparent red solution. Solution B: K<sub>3</sub>[Co(CN)<sub>6</sub>]<sub>2</sub> (16.6 mg, 0.04 mmol) and PVP surfactant (0.3 g) were dissolved in distilled water (10 mL). Solution A was slowly and regularly added to solution B through a syringe to form a red colloid solution. The whole reaction was performed at room temperature with agitated stirring. After 10 min, the reaction was aged for 24 h at room temperature without any interruption. The resulting pink-colored precipitate was filtered and washed several times with distilled water and finally dried in air at 60 °C.

## Material characterization:

The powder XRD patterns of the samples were recorded with an X-ray diffractometer (Japan Rigaku D/MAX- $\gamma$ A) using Cu-Ka radiation ( $\lambda$ =1.54178 A) with 20 range of 10–70°. FESEM images were taken on a JEOL JSM-6700 M scanning electron microscope. TEM images were collected from Hitachi H-800 transmission electron microscope using an accelerating voltage of 200 kV, and a HRTEM (JEOL-2011) was operated at an accelerating voltage of 200 kV. TGA of Fe<sub>3</sub> [Co(CN)<sub>6</sub>]<sub>2</sub> was carried out using a Shimadzu-50 thermoanalyser under flowing nitrogen and at a heating rate of 10°Cmin<sup>-1</sup>. XPS was performed on an ESCALAB 250 X-ray photoelectron spectrometer using Al Ka radiation. The specific surface area was evaluated at 77 K (Micromeritics ASAP 2020) using the Brunauer–Emmett–Teller (BET) method applied to the adsorption branch.

## **Calculation details:**

We perform DFT calculations using the Vienna Ab Initio Simulation Package (VASP),<sup>2,3</sup> the generalized gradient approximation (GGA) of Perdew–Becke–Ernzerhof (PBE) is used for the exchange-correlation functional.<sup>4</sup> The cut-off energies for plane waves is 400 eV, providing a convergence of  $10^{-5}$  eV in total energy and 0.02 eV/Å in Hellmann Feynman force on each atom. All of the models are calculated in a periodically repeated slab with a dimension of 12.3 Å × 12.3Å × 20.0 Å to separate the interaction between periodic images. The Gama scheme with 2×2×1 K-point mesh is used to represent the Brillouin zone. The free energy of the adsorbed state is calculated as

 $\Delta G_{H^*} = \Delta E_{H^*} + \Delta E_{ZPE} \text{ - } T\Delta S$ 

where  $\Delta E_{H^*}$  is the hydrogen chemisorption energy, and  $\Delta E_{ZPE}$  is the difference corresponding to the zero point energy between the adsorbed state and the gas phase. As the vibrational entropy of H\* in the adsorbed state is small, the entropy of adsorption of  $\frac{1}{2}$ H<sub>2</sub> is  $\Delta S_{H} \approx -\frac{1}{2}S_{0H_2}$ , where S<sub>0H2</sub> is the entropy of H<sub>2</sub> in the gas phase at the standard conditions. Therefore the overall corrections are taken as in<sup>5,6</sup>

 $\Delta G_{\rm H*} = \Delta E_{\rm H*} + 0.24 \ eV$ 

## **Electrochemical measurement details:**

All of the electrochemical measurements were performed in a three-electrode system on an electrochemical workstation (CHI 660D) in 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte. Typically, 4 mg of catalyst and 30 $\mu$ L Nafion solution (Sigma Aldrich, 5 wt %) were dispersed in 1 mL ethanol solution by sonicating for 1 h to form a homogeneous ink. Then 5  $\mu$ L of the dispersion (containing 20  $\mu$ g of catalyst) was loaded onto a glassy carbon electrode with 3 mm diameter (loading 0.285 mg cm<sup>-2</sup>). While a Ag/AgCl (in 3 M KCl solution) electrode and a platinum foil were served as the reference electrode and counter electrodes, respectively. All of the potentials were calibrated to a reversible hydrogen electrode (RHE). The working electrode was polished with Al<sub>2</sub>O<sub>3</sub> powders with size down to 0.05  $\mu$ m. Commercial Pt/C catalysts (E-TEK, Pt: 40 % wt) were used as a reference to evaluate the electrocatalytic performance of various samples. Hundreds of potential cycles were conducted in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution with continuous N<sub>2</sub> gas in the potential region from 0.05 to 1.05 V at a sweep rate of 50 mVs<sup>-1</sup> till the cyclic voltammetry curves (CVs) stay unchanged, in order to let residue organics and ions release. Linear sweep voltammetry with a scan rate of 2 mV s<sup>-1</sup> was conducted with a flow of N<sub>2</sub> gas maintained over the electrolyte during the HER experiment to eliminate dissolved oxygen. Cyclic voltammetry (CV) was conducted between -0.3 and 0.1 V versus RHE for 10000 times to investigate the cycling stability.

The electrochemically active surface area (ECSA) of samples was usually estimated using a simple cyclic voltammetry method.<sup>7</sup> The ECSA of a catalyst sample is calculated from the double layer capacitance according to following formula:

## $ECSA=C_{dl}/C_s$

However, solving for the exact surface area of our material is difficult due to the unknown capacitive behavior ( $C_s$ ) of the FeCo alloy electrode especially with carbon shell. But we can safely estimate relative surface areas of three samples, since the double layer capacitance ( $C_{dl}$ ) is expected to be linearly proportional to effective active surface area for samples with similar composition and this method was also employed in previous study.<sup>8</sup> The double layer capacitance is estimated by plotting the  $\Delta J$  at 0.15 V vs RHE against the scan rate, where the slope is twice of  $C_{dl}$ . The results showed that  $C_{dl}$  of S-600, S-700 and S-800 were 6.0, 5.4 and 3.2 mF/cm<sup>2</sup> respectively.

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