## **Supporting Information**

A Novel Flower-Like Architecture of FeCo@NC Functionalized Ultra-Thin Carbon Nanosheets as Highly Efficient 3D Bifunctional Electrocatalyst for Full Water Splitting

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#### **1. Experimental Section.**

# **1.1** Synthesis of 3D PVP/Fe(AC)<sub>2</sub>, PVP/Co(AC)<sub>2</sub>, and PVP/[Fe(AC)<sub>2</sub>]<sub>x</sub>/[Co(AC)<sub>2</sub>]<sub>y</sub> (*x*+*y*=1) networks.

All chemicals were used as received without further purification. As shown in **Scheme 1**, in a typical procedure, 0.8 g polyvinyl alcohol (PVP, Mw = 90000, Sinopharm Chemical Reagent) powders were dissolved into 10.0 mL N-N-dimethylformamide (DMF) to produce a homogeneous PVP-DMF slurry. After 0.4 g of metal acetate  $[M(C_2H_3O_2)_2 4H_2O; M=Fe \text{ or } Co]$  or stoichiometric  $[Fe(AC)_2]_x/[Co(AC)_2]_y$  (x+y=1) were added into the PVP-DMF slurry, the resultant mixtures were further stirred for 6 h to prepare the homogeneous [*i.e.* **PVP-Fe(AC)\_2**, **PVP-Co(AC)\_2**, **and PVP-[Fe(AC)\_2]\_x-[Co(AC)\_2]\_y** (x+y=1)] precursor slurries. The obtained precursor solution was loaded into the plastic syringes with the inner diameters of pinhead at 0.80 mm. A voltage of 25 kV was applied for electrospinning with a flow rate of 1 mL h<sup>-1</sup>. The stainless steel mesh was used to collect the **PVP/Fe(AC)\_2**, **PVP/Co(AC)\_2**, **and PVP/[Fe(AC)\_2]\_x/Co(AC)\_2]\_y** (x+y=1)] precursor networks. The distance between the orifice and the stainless steel mesh electrode was ~15 cm.

# **1.2** Synthesis of Fe<sub>4</sub>N@NC/NCNF-800, Co@NC/NCNS-800, Fe<sub>x</sub>Co<sub>y</sub>@NC/NCNS-800 (x+y=1), and Fe<sub>0.5</sub>Co<sub>0.5</sub>@NC/NCNS-*T* (*T*=600, 700, 800, 900, and 1000 °C) catalysts.

Following closely, those as-electrospun 3D PVP/Fe(AC)<sub>2</sub>, PVP/Co(AC)<sub>2</sub>, and PVP/[Fe(AC)<sub>2</sub>]<sub>x</sub>/[Co(AC)<sub>2</sub>]<sub>y</sub> (x+y=1) networks were carbonized at 800 °C with a heating rate of 5 °C min<sup>-1</sup> for 2 h in NH<sub>3</sub> atmosphere to obtain the desired Fe<sub>4</sub>N@NC/NCNF-800, Co@NC/NCNS-800, and Fe<sub>x</sub>Co<sub>y</sub>@NC/NCNS-800 (x+y=1) catalysts. It's important to note that as the sample just containing Fe is of 3D networks composed by some 1D nanofibers (NFs) after pyrolyzing at 800 °C and the as-appeared Fe<sub>4</sub>N particles are embedded into the carbon shells (proved by XRD test). Thus, the resultant samples involving Fe is recorded as Fe<sub>4</sub>N@NC/NCNF-800 networks in this study. However, all hybrids involving Co are carbon nanosheets based compounds after heating procedures, and only metallic Co or Co based alloys are measured in XRD patterns. Thus, those Co based samples are denoted as Fe<sub>x</sub>Co<sub>y</sub>@NC/NCNS-*T*, where *x* and *y* values represent the molar percentages of Fe

and Co tested by XRD (x+y=1, x values have been controlled as 0.7, 0.5, 0.3, and 0 accompanied by the change of y from 0.3 to 1 respectively). Nevertheless, the T values represent the calcination temperatures of the as-electrospun PVP/[Fe(AC)<sub>2</sub>]<sub>0.5</sub>/[Co(AC)<sub>2</sub>]<sub>0.5</sub> networks, which were calcinated at different carbonization temperatures from 600 to 1000 °C for 2 h in NH<sub>3</sub>.

#### 1.3 Physical characterization of resultant catalysts.

Wide-angle XRD patterns were obtained on an X-ray D/max-2200 vpc (Rigaku Corporation, Japan) instrument operated at 40 kV and 20 mA using Cu Ka radiation (k 0.15406 nm). SEM images were performed using a Philips XL-30 ESEM. TEM analysis was performed on a high-resolution Hitachi JEM-2100 system equipped with an EDX analyzer. Surface chemical analysis of resultant catalysts was carried out by XPS spectra recorded on an ESCA LAB spectrometer (USA) using a monochromatic Al K $\alpha$  source (hv 1486.6 eV). The binding energies were calibrated by using the containment carbon (C 1s 284.6 eV). N2 adsorption-desorption isotherms were performed on an ASAP 2020 (Micromeritics, USA). Before the measurements, the samples were degassed in vacuum at 150 °C for 6 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the BET specific surface area by using adsorption data. The pore size distribution was derived from the adsorption branch by using the Barrett-Joyner-Halenda (BJH) model. Raman spectra were obtained using a confocal microprobe Raman system (HR800, JobinYvon). Fe and Co contents of catalysts were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) with a PerkinElmer Optima 3300 DV spectrometer.

#### **1.4 Electrochemical characterization methods**

All electrochemical measurements were performed with a standard three-electrode cell at room temperature by using a rotating disk electrode (RDE; 5 mm in diameter) modified by catalysts as working electrode. Ag/AgCl (saturated KCl) was used as reference electrode and Pt wire was used as counter electrode for OER test. To avoid any possible contamination of Pt, the carbon rod was used as counter electrode for exploring the HER catalytic activities of catalysts. All potentials appeared in this paper are referred to reversible hydrogen electrode (RHE; the potentials recorded and referred to RHE in each experiment were calculated by using the formula  $E_{RHE} = E_{Ag/AgCl} + 0.059 \text{ pH} + 0.059 \text{ pH}$ 

0.197 V, where  $E_{RHE}$  is a potential *vs.* RHE,  $E_{Ag/AgCl}$  is a potential *vs.* Ag/AgCl (saturated KCl), and pH is the pH value of electrolyte. All current densities are the ratios of recorded currents to the geometric area of electrode. The onset potentials were determined from the intersection of the tangents of OER/HER current and the polarization curve baseline. The resistance of the electrolytes was measured and the voltammograms were recorded with *iR* drop compensation unless specifically mentioned.

In order to prepare the working electrodes, 3 mg of catalyst powders were firstly dispersed in 1 mL Nafion solution (0.5 *wt.*%) with 45 min of ultrasonication to generate homogeneous inks. Next, 30 uL of the dispersion was transferred onto GCE with the catalyst loading amount of 0.306 mg cm<sup>-2</sup>. Finally, the as-prepared catalyst film was dried at room temperature.

In the electrochemical testing processes for HER and OER; the polarization curves were also plotted as potential (*E vs. RHE*) *versus*  $\log |j|$  mA cm<sup>-2</sup> to get the Tafel plots for assessing the HER and OER kinetics of the resultant catalysts. By fitting the linear portion of Tafel plots to the Tafel equation ( $\eta = b \log (j) + a$ ), the Tafel slope (*b* values) can be obtained. All LSV data referring to HER and OER were reported with the *iR*-compensation.

We further quantitatively measured the generated  $O_2$  and  $H_2$  amounts by using calibrated pressure sensors to monitor the pressure changes at both anode and cathode compartments of H-type electrolytic cells, respectively. The Faradic efficiency (FE) for both processes was calculated by comparing the experimentally quantified  $O_2$  and  $H_2$  amounts with the theoretically calculated  $O_2$  and  $H_2$  amounts (assuming 100% FE).

- 2. Morphologies and structures of resultant samples.
- 2.1 Morphologies of different 3D precursor networks observed by SEM images.



**Figure S1** SEM images of the as-electrospun (a) PVP/Fe(AC)<sub>2</sub>, (b) PVP/Fe(AC)<sub>2</sub>/Co(AC)<sub>2</sub> (Fe: Co=0.7: 0.3), (c) PVP/Fe(AC)<sub>2</sub>/Co(AC)<sub>2</sub> (Fe: Co=0.5: 0.5), (d) PVP/Fe(AC)<sub>2</sub>/Co(AC)<sub>2</sub> (Fe: Co=0.3: 0.7), and (e) PVP/Co(AC)<sub>2</sub> precursor networks.

2.2 Morphologies and structures of the resultant samples calcined at 800  $^{\rm o}{\rm C}$  by SEM and TEM images.



Figure S2 SEM images of resultant (a)  $Fe_4N@NC/NCNF-800$ , (b)  $Fe_{0.7}Co_{0.3}@NC/NCNS-800$ , (c)  $Fe_{0.3}Co_{0.7}@NC/NCNS-800$ , and (d) Co@NC/NCNS-800 samples. TEM images of resultant (a')  $Fe_4N@NC/NCNF-800$ , (b')  $Fe_{0.7}Co_{0.3}@NC/NCNS-800$ , (c')  $Fe_{0.3}Co_{0.7}@NC/NCNS-800$ , and (d') Co@NC/NCNS-800 samples.

The metal salts used in precursors directly control the morphologies and structures of resultant samples. After the typical pyrolysis processes at 800  $\,^{\circ}$ C with a heating rate of 5  $\,^{\circ}$ C min<sup>-1</sup> for 2 h in the NH<sub>3</sub> atmosphere, huge changes have taken place in morphologies and structures of resultant both the samples. For the Fe<sub>4</sub>N@NC/NCNF-800 sample without using any Co source, both the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images display the formation of the typical 3D networks (Figures S2a and S2a'), which is similar to the overall morphology of precursor films. Nevertheless, the biggest difference is that vast nanoparticles (NPs) have dispersed along with each 1D CNF. What is surprising is that once 30% of Fe(AC)<sub>2</sub> were replaced by Co(AC)<sub>2</sub> in the precursor slurry, both the morphology and structure of Fe<sub>0.7</sub>Co<sub>0.3</sub>@NC/NCNS-800 change obviously. One can see that most 1D CNFs disappear; instead, the rudiment of 3D hierarchical porous architecture appears (Figure S2b) and abundant NPs are encapsulated within the graphene layers (Figure S2b'). Sequentially increasing the Co(AC)<sub>2</sub> dosage to 50 % in the precursor slurry, an interconnected 3D porous configuration have been synthesized with the layered and crumpled walls for Fe<sub>0.5</sub>Co<sub>0.5</sub>@NC/NCNS-800 (Figures 1b-d). Meanwhile, the amplification TEM image shown in **Figure 1e** further confirms the uniform distribution of vast tiny nanocrystals with the particle diameters distributed in the range of 5-30 nm (the average diameter is 18.98 nm). Upon sequentially increasing the dosage of  $Co(AC)_2$  content in precursor slurries, the thickness of Fe<sub>0.3</sub>Co<sub>0.7</sub>@NC/NCNS-800 increases with the disappearance of vast porous channels (Figures S2c-c'). Particularly, for the Co@NC/NCNS-800 sample, although the layer-like CNSs still exist, the thickness of each nanosheet is much larger than other CNSs mentioned above (Figures S2d-2d'). Specially, those open channels nearly disappear with larger-sized and irregular NPs distributing on the surfaces. In view of the structural integrity of 3D hierarchically porous architectures, x=0.5 is the best choice for preparing the ideal FeCo@NC/NCNS sample with fine FeCo@C units dispersing on its surfaces.

**2.3** Morphologies and structures of the resultant  $Fe_{0.5}Co_{0.5}@NC/NCNS-T$  samples calcined at different temperatures by SEM images.



Figure S3 SEM images of the resultant (a)  $Fe_{0.5}Co_{0.5}@NC/NCNS-600$ , (b)  $Fe_{0.5}Co_{0.5}@NC/NCNS-700$ , (c)  $Fe_{0.5}Co_{0.5}@NC/NCNS-900$ , and (d)  $Fe_{0.5}Co_{0.5}@NC/NCNS-1000$  samples calcined at different temperatures.

It is well known that pyrolysis temperature also hugely impacts the morphologies, structures, chemical compositions, and even the catalytic activities of resultant catalysts. When the annealing temperature was fixed at 600 °C, SEM image of Fe<sub>0.5</sub>Co<sub>0.5</sub>@NC/NCNS-600 cannot show either the typical nanosheet-like structures or the obviously porous structures. The surfaces of Fe<sub>0.5</sub>Co<sub>0.5</sub>@NC/NCNS-600 are relatively smooth and just a little NPs can be seen (**Figure S3a**). However, when increasing the final carbonization temperature to 700 °C, the resultant Fe<sub>0.5</sub>Co<sub>0.5</sub>@NC/NCNS-700 hybrid sample shows the typical porous channels stacking by vast CNSs (**Figure S3b**). Furthermore, there are abundant obvious and tiny NPs can be seen on the surfaces. When a carbonization temperature of 800 °C, those layered and crumpled CNSs have assembled into the 3D hierarchically

meso/macroporous configurations for resultant Fe0.5Co0.5@NC/NCNS-800 hybrid sample (Figures 1b-d). What is more important is that large amount of FeCo NPs have uniformly embedded into 8-10 carbon layers and built vast electrochemical active FeCo@C units. These structural characteristics are all contributed to boosting the electrocatalytic activity. At a higher pyrolysis temperature of 900 °C (Figure S3c), compared with Fe<sub>0.5</sub>Co<sub>0.5</sub>@NC/NCNS-800, the 3D hierarchically porous scaffolding remains in place during pyrolysis process for Fe<sub>0.5</sub>Co<sub>0.5</sub>@NC/NCNS-900. Although the nanosheet-like carbon frameworks do not collapse, these CNSs still appear a shrink that directly lead to the exposure of abundant large-sized NPs on surfaces. Finally, once we continue to increase the calcination temperature to 1000  $\,$   $\,$   $\,$   $\,$  one can see that almost all 3D porous channels disappear for resultant Fe0.5Co0.5@NC/NCNS-1000 because of the drastic pyrolysis and contraction of precursor networks (Figure S3d). All in all, a pyrolysis temperature of 800 °C is more beneficial to construct the 3D hierarchically porous architectures.

After various controlling experiments, summarizing the SEM and TEM characterization results, the dosages of  $Fe(AC)_2$  and  $Co(AC)_2$  together with calcination temperature all impact morphologies and structures of resultant products. One can see that at the optimal temperature of 800 °C, co-existence of the same number of  $Fe(AC)_2$  and  $Co(AC)_2$  is the key factor to forming the 3D hierarchically meso/macroporous M@NC/NCNS architectures with abundant M@NC units uniformly dispersing on their surfaces. Only adopting  $Fe(AC)_2$  have resulted in the 3D networks but only using  $Co(AC)_2$  can only bring about the growth of thick CNSs. Upon stoichiometric ratios of  $Co(AC)_2$  and  $Fe(AC)_2$  are the same in the synthetic system, thin CNSs with vast small-sized FeCo@NC units dispersed on the surfaces can be produced and assemble into the 3D hierarchically meso/macroporous configurations. Either increasing the quantity of  $Co(AC)_2$  or  $Fe(AC)_2$  will break the balance, leading to the structural damage of 3D hierarchically meso/macroporous FeCo@NC/NCNS.

2.4 The central role of electrospinning technology in adjusting the morphologies and structures of resultant sample by SEM and TEM images.



**Figure S4** SEM (a) and TEM (b) images of  $Fe_{0.5}Co_{0.5}@NC-800$  sample synthesized from the PVP/Fe(AC)<sub>2</sub>/Co(AC)<sub>2</sub> (Fe(AC)<sub>2</sub>: Co(AC)<sub>2</sub>=1: 1) precursor without the electrospinning processes in NH<sub>3</sub> at 800 °C.

One can see from SEM (**Figure S4a**) image that  $Fe_{0.5}Co_{0.5}@NC-800$  sample consists of vast bulks, although it's TEM (**Figure S4b**) image shows abundant mesopores on the surfaces. These results powerfully prove the central roles of electrospinning technology in constructing the 3D porous flower-like architectures consist of 2D thin and porous carbon nanosheets.

#### 2.5 XRD characterizations for as-prepared samples.



**Figure S5** Amplification of XRD (110) peak (**a**), (200) peak (**b**), and (211) peak (**c**) for the resultant Fe<sub>0.7</sub>Co<sub>0.3</sub>@NC/NCNS-800 (**a1**, **b1**, **c1**), Fe<sub>0.5</sub>Co<sub>0.5</sub>@NC/NCNS-800 (**a2**, **b2**, **c2**), and Fe<sub>0.3</sub>Co<sub>0.7</sub>@NC/NCNS-800 (**a3**, **b3**, **c3**) samples.

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**Figure S6** Survey XRD patterns (**a**), amplification of XRD (110) peak (**b**), (200) peak (**c**), and (211) peak (**d**) of the Fe<sub>0.5</sub>Co<sub>0.5</sub>@NC/NCNS-*T* samples (T= 600, 700, 800, 900, and 1000).

The results of XRD characterizations for  $Fe_{0.5}Co_{0.5}@NC/NCNS-T$  samples (*T*= 600, 700, 800, 900, and 1000) got at different calcining temperatures are shown in **Figure S6**. It is clear that only the XRD diffraction peaks in regard to the FeCo alloy can be observed. Even so, seeing from the amplification of XRD (110), (200), and (211) planes of the  $Fe_{0.5}Co_{0.5}@NC/NCNS-T$  samples (**Figures S6**), it can be observed that the XRD peak intensity of (110), (200), and (211) planes for each sample increases rapidly with rise in the final pyrolysis temperature from 600 to 800 °C.  $Fe_{0.5}Co_{0.5}@NC/NCNS-600$  and  $Fe_{0.5}Co_{0.5}@NC/NCNS-700$  all display the weak (110), (200), and (211) planes but the  $Fe_{0.5}Co_{0.5}@NC/NCNS-800$  shows the sharp diffraction peaks of CoFe alloy. Furthermore, when the final pyrolysis temperature increases to

900 or 1000 °C, both peak positions and intensities of resultant  $Fe_{0.5}Co_{0.5}@NC/NCNS-900$  and  $Fe_{0.5}Co_{0.5}@NC/NCNS-1000$  samples are similar to those for  $Fe_{0.5}Co_{0.5}@NC/NCNS-800$ . In other words, 800 °C has already met the requirements for synthesizing perfect CoFe alloy NPs and then constructing the ideal FeCo@NC units in the catalyst systems.





Figure S7 (a) BET surface area distribution histograms of  $Fe_4N@NC/NCNF-800$  (a1),  $Fe_{0.7}Co_{0.3}@NC/NCNS-800$  (a2),  $Fe_{0.5}Co_{0.5}@NC/NCNS-800$  (a3),  $Fe_{0.3}Co_{0.7}@NC/NCNS-800$  (a4) and Co@NC/NCNS-800 (a5). The typical pore size distribution curves calculated by using the BJH method for resultant  $Fe_4N@NC/NCNF-800$  (b), Co@NC/NCNS-800 (c),  $Fe_{0.7}Co_{0.3}@NC/NCNS-800$  (d), and  $Fe_{0.3}Co_{0.7}@NC/NCNS-800$  (e) samples.

In order to further determine the porosity of as-prepared materials, N<sub>2</sub> adsorption-desorption isothermal analyses were first performed and recorded in Figure 2b. As shown in Figure S7a, the specific Brunauer-Emmett-Teller (BET) surface area of Fe<sub>0.5</sub>Co<sub>0.5</sub>@NC/NCNS-800 is as large as 440.9 m<sup>2</sup> g<sup>-1</sup>, which is much larger than those of Fe<sub>4</sub>N@NC/NCNF-800 (346.8 m<sup>2</sup> g<sup>-1</sup>), Fe<sub>0.7</sub>Co<sub>0.3</sub>@NC/NCNS-800  $(390 \text{ m}^2 \text{ g}^{-1})$ , Fe<sub>0.3</sub>Co<sub>0.7</sub>@NC/NCNS-800 (281.2 m<sup>2</sup> g<sup>-1</sup>), and Co@NC/NCNS-800  $(237.3 \text{ m}^2 \text{ g}^{-1})$ . The huge differences in BET surface areas of different samples can be explained by their pore size distribution (PSD) curves as shown in Figure 2b and Figures S7b-e. As can be seen from Figure S7a, once changing the metal salts in the precursors, even if adopting the same synthetic steps, Fe<sub>4</sub>N@NC/NCNF-800 shows larger BET surface area than that of Co@NC/NCNS-800. One can see from Figure S7b that large amount of mesopores located between 2-10 nm have dispersed along with the 3D hierarchically porous structures of Fe<sub>4</sub>N@NC/NCNF-800 accompanying some stacking pores of CNFs between 10-100 nm. However, the Co@NC/NCNS-800 sample mainly displays the larger pores between 10-100 nm, those mesopores between 2-10 nm are inadequate for Co@NC/NCNS-800 (Figure S7c). The  $Fe_{0.7}Co_{0.3}$ @NC/NCNS-800 controls a larger BET surface area of 390 m<sup>2</sup> g<sup>-1</sup> than the above mentioned two samples. One can see from Figure S7d that the numbers of mesopores located between 2-10 nm have increased radically for Fe<sub>0.7</sub>Co<sub>0.3</sub>@NC/NCNS-800. That is why Fe<sub>0.7</sub>Co<sub>0.3</sub>@NC/NCNS-800 sample owns the larger BET area. Fe<sub>0.5</sub>Co<sub>0.5</sub>@NC/NCNS-800 has the largest BET surface area among all samples. Both SEM and TEM images (Figures 1b-g) have revealed that Fe0.5Co0.5@NC/NCNS-800 possesses the most excellent 3D hierarchical porous channels with abundant mesopores (2-10 nm) dispersed on surfaces. In fact, PSD curve of Fe<sub>0.5</sub>Co<sub>0.5</sub>@NC/NCNS-800 (Figure 2b) demonstrates the presence of vast mesopores located between 2-10 nm and stacking pores of CNS between 10-100 nm. Above all, the amount of mesopores between 2-10 nm is much larger than other reference samples for Fe0.5Co0.5@NC/NCNS-800, thus its BET surface area is the maximum. However, Fe<sub>0.3</sub>Co<sub>0.7</sub>@NC/NCNS-800 (Figure S7e) does not show obvious pores distributed between 2-10 nm and most mesopores between 3-6 nm even





**Figure S8 (a)** N<sub>2</sub> adsorption–desorption isotherms and **(b)** the corresponding BET surface area distributions of the Fe<sub>0.5</sub>Co<sub>0.5</sub>@NC/NCNS-*T* (*T*= 600, 700, 800, 900, and 1000  $^{\circ}$ C) samples.

When changing the calcination temperature, only the  $Fe_{0.5}Co_{0.5}@NC/NCNS-800$  material shows isotherm profiles characteristic of type IV with the hysteresis loops (**Figure S8a**), demonstrating the mesoporous structures. However, the isotherm profiles of other materials can be categorized as being of type I, indicating the insufficient of mesoporous structures for these materials. More interestingly, BET surface area is found to increase with pyrolysis temperature from 600 to 800 °C and then decrease on the contrary with pyrolysis temperature from 800 to 1000 °C (as shown in **Figure S8b**).



2.7 Investigating the structures of the resultant compounds by Raman spectra.

**Figure S9** Raman spectra of the resultant  $Fe_4N@NC/NCNF-800$  (a), Co@NC/NCNS-800 (b),  $Fe_{0.7}Co_{0.3}@NC/NCNS-800$  (c), and  $Fe_{0.3}Co_{0.7}@NC/NCNS-800$  (d) hybrid compounds.



**Figure S10** Raman spectra of  $Fe_{0.5}Co_{0.5}@NC/NCNS-T$  (*T*=600, 700, 800, 900, and 1000 °C) materials (**a-e**). (**f**) The  $I_D/I_G$  values calculated from the D-peak area and G peak area fitted for different  $Fe_{0.5}Co_{0.5}@NC/NCNS-T$  hybrids ( $I_D/I_G$  = D-peak area/G peak area).

# **2.8** Testing and comparing the contents of each N based species for all control materials by fitting their high resolution N 1s XPS spectra.

	N1	N2	N3	N4	N5	Total
Samples	Pyridinic	Pyridinic M-N		Graphitic	Oxidized	Ν
	N (at.%)	(at.%)	N (at.%)	N (at.%)	N (at.%)	(at.%)
Fe <sub>4</sub> N@NC/NCNF-800	0.962	0.256	0.768	1.636	0.508	4.13
Fe <sub>0.7</sub> C0 <sub>0.3</sub> @NC/NCNS-800	1.663	0.353	0.990	0.628	0.944	4.58
Fe <sub>0.5</sub> Co <sub>0.5</sub> @NC/NCNS-800	1.627	0.537	0.490	1.742	0.327	4.67
Fe <sub>0.3</sub> Co <sub>0.7</sub> @NC/NCNS-800	1.322	0.684	1.277	0.958	0.319	4.56
Co@NC/NCNS-800	0.990	0.326	1.544	0.740	0.630	4.23

**Table S1** A comparison in the contents of Pyridinic N, M-N, Pyrrolic N, Graphitic N, and oxidized N species for resultant catalysts calculated from the N 1s spectra.



Figure S11 Chemical binding states of N 1s for different samples. (a)  $Fe_4N@NC/NCNF-800$ , (b)  $Fe_{0.7}Co_{0.3}@NC/NCNS-800$ , (c)  $Fe_{0.5}Co_{0.5}@NC/NCNS-800$ , (d)  $Fe_{0.3}Co_{0.7}@NC/NCNS-800$ , and (e) Co@NC/NCNS-800. (f) The comparison of Pyridinic N, M-N, Pyrrolic N, Graphitic N, and oxidized N species for different samples. Different samples in Figure S11f are  $Fe_4N@NC/NCNF-800$  (1),  $Fe_{0.7}Co_{0.3}@NC/NCNS-800$  (2),  $Fe_{0.5}Co_{0.5}@NC/NCNS-800$  (3),  $Fe_{0.3}Co_{0.7}@NC/NCNS-800$  (4), and Co@NC/NCNS-800 (5).



**Figure S12** Chemical binding state of N 1s for different samples pyrolyzed at different temperatures. (a)  $Fe_{0.5}Co_{0.5}@NC/NCNS-700$ , (b)  $Fe_{0.5}Co_{0.5}@NC/NCNS-900$ , and (c)  $Fe_{0.5}Co_{0.5}@NC/NCNS-1000$ . (d) The percentages of Pyridinic N, M-N, Pyrrolic N, Graphitic N, and oxidized N species for different  $Fe_{0.5}Co_{0.5}@NC/NCNS-T$  samples.

	Pyridinc N	M-N	Pyrrolic	Graphitic	Oxidized	
	(at.%)	(at.%)	N (at.%)	N (at.%)	N (at.%)	
Fe0.5Co0.5@NC/NCNS						
-700	20.5	11	30.8	13.7	24	
Fe0.5Co0.5@NC/NCNS						
-800	34.7	11.5	10.5	37.3	7	
Fe0.5Co0.5@NC/NCNS						
-900	23.8	11.7	12.3	39.9	12.3	
Fe0.5Co0.5@NC/NCNS						
-1000	11.7	21.7	15	41.6	10	

**Table S2** A comparison in contents of Pyridinic N, M-N, Pyrrolic N, Graphitic N, and oxidized N species for resultant  $Fe_{0.5}Co_{0.5}@NC/NCNS-T$  catalysts calculated from their N 1s spectra.

**2.9** Testing and comparing the existent forms of metal elements in all control materials by fitting their high resolution Fe 2p, and Co 2p XPS spectra.



Figure S13 High-resolution Fe 2p spectra of (a)  $Fe_4N@NC/NCNF-800$ , (b)  $Fe_{0.7}Co_{0.3}@NC/NCNS-800$ , (c)  $Fe_{0.5}Co_{0.5}@NC/NCNS-800$ , and (d)  $Fe_{0.3}Co_{0.7}@NC/NCNS-800$  samples. High-resolution Co 2p spectra of (e) Co@NC/NCNS-800, (f)  $Fe_{0.7}Co_{0.3}@NC/NCNS-800$ , (g)  $Fe_{0.5}Co_{0.5}@NC/NCNS-800$ , and (h)  $Fe_{0.3}Co_{0.7}@NC/NCNS-800$  samples.

### **3. OER electrocatalytic activity evaluation for resultant materials in 1.0 M KOH solution.**

3.1 CV tests of resultant materials in 1.0 M KOH solution.



**Figure S14** Cyclic Voltammetry (CV) curves recorded at a scan rate of 50 mV s<sup>-1</sup> between 0 and 1.5 V *vs.* RHE in 1.0 M KOH solution for (**a**) Fe<sub>4</sub>N@NC/NCNF-800, (**b**) Fe<sub>0.7</sub>Co<sub>0.3</sub>@NC/NCNS-800, (**c**) Fe<sub>0.5</sub>Co<sub>0.5</sub>@NC/NCNS-800, (**d**) Fe<sub>0.3</sub>Co<sub>0.7</sub>@NC/NCNS-800, (**e**) Co@NC/NCNS-800 samples.

Figure S14 shows CV curves of various materials in 1.0 M KOH. No obvious redox peaks have been observed in CV plot of Fe<sub>4</sub>N@NC/NCNF-800 and only a typical capacitive current is observed for it (Figure S14a). Nevertheless, a pair of redox peaks assigned to the redox couple of Fe(II)/Fe(III) can be observed around 0.6 V Fe0.7Co0.3@NC/NCNS-800 vs. RHE for (Figure **S14b**) and Fe<sub>0.5</sub>Co<sub>0.5</sub>@NC/NCNS-800 (Figure S14c), but which cannot be seen in CV curve of Fe<sub>0.3</sub>Co<sub>0.7</sub>@NC/NCNS-800 (Figure S14d). In addition, upon adopting Co sources in the precursor slurries, another pair of redox peaks located between 0.7 and 0.9 V vs. RHE simultaneously appear in CV curves of Fe<sub>0.7</sub>Co<sub>0.3</sub>@NC/NCNS-800, Fe<sub>0.5</sub>Co<sub>0.5</sub>@NC/NCNS-800, and Fe<sub>0.3</sub>Co<sub>0.7</sub>@NC/NCNS-800 materials (Figures S14b-d), which are assigned to the redox couple of Co(0)/Co(II). Meantime, the redox peaks of Co(II)/Co(III) can also be observed in CV curves of Fe<sub>0.7</sub>Co<sub>0.3</sub>@NC/NCNS-800, Fe<sub>0.5</sub>Co<sub>0.5</sub>@NC/NCNS-800, Fe<sub>0.3</sub>Co<sub>0.7</sub>@NC/NCNS-800, and Co@NC/NCNS-800 (Figures S14b-e). It's worth noting that redox peaks of Co(II)/Co(III) in CV curve of  $Fe_{0.5}Co_{0.5}@NC/NCNS-800$  is overlapped with the redox peaks of Co(III)/Co(IV). Finally, except for  $Fe_{0.7}Co_{0.3}@NC/NCNS-800$ , redox peaks of the redox couple of Co(III)/Co(IV) are existed in CV curves of other Co based samples. Specially, the CV tests indicate that all FeCo@NC/NCNS-800 samples show much larger electroactive areas than those of  $Fe_4N@NC/NCNF-800$  and Co@NC/NCNS-800. All the above results prove the ultra-strongly synergistic effect between Co and Fe. In conclusion, the redox current peaks attributed to the reversible reaction between Fe(II)/Fe(III), Co(0)/Co(II), and Co(III)/Co(IV) can be clearly observed in CV curve of  $Fe_{0.5}Co_{0.5}@NC/NCNS-800$ . Meanwhile, the largest integral area of CV curve for  $Fe_{0.5}Co_{0.5}@NC/NCNS-800$  also demonstrates its largest electrochemical active area.

**3.2 LSV curves, Tafel plots, and EIS Nyquist plots recorded for testing OER performances of different samples.** 



**Figure S15** (a) OER Polarization curves, (b) comparison of potentials recorded at 10 mA cm<sup>-2</sup>, (c) Tafel plots, and (d) EIS Nyquist plots recorded at 1.60 V of the Fe<sub>0.5</sub>Co<sub>0.5</sub>@NC/NCNS-*T* (T = 600, 700, 800, 900 and 1000 °C) catalysts, The semicircles in the Nyquist plots are attributed to the charge-transfer resistance ( $R_{ct}$ ) and are related to the electrocatalytic kinetics. A lower  $R_{ct}$  value corresponds to a faster reaction rate.

Catalysts	$E_{10}$	Tafel slop	References		
Fe <sub>4</sub> N@NC/NCNF-800	1.736	85.35			
Fe <sub>0.7</sub> Co <sub>0.3</sub> @NC/NCNS-800	1.564	61.64			
Fe <sub>0.5</sub> Co <sub>0.5</sub> @NC/NCNS-800	1.500	50.19	This work		
Fe <sub>0.3</sub> Co <sub>0.7</sub> @NC/NCNS-800	1.614	69.12			
Co@NC/NCNS-800	1.653	62.87			
RuO <sub>2</sub>	1.558	47.6			
Ni–P	1.53	64	Energy Environ. Sci. 2016, 9, 1246-1250		
CoP/rGO	1.57	66	Chem. Sci. 2016, 7, 1690–1695		
Ni <sub>3</sub> Se <sub>2</sub> –GC	1.54	79.5	Energy Environ. Sci. 2016, 9, 1771-1782		
CP/CTs/Co-S	1.536	72	ACS Nano 2016, 10, 2342-2348		
NCNT/Co <sub>x</sub> Mn <sub>1-x</sub> O	1.57	40	Nano Energy 2016, 20, 315–325		
Co@Co <sub>3</sub> O <sub>4</sub> /NC (0.1 M KOH)	1.64	54.3	Angew. Chem. Int. Ed. 2016, 55,4087-4091		
CoP/Carbon Cloth	1.511	-	ChemSusChem 2016, 9, 472–477		
CoPi	1.61	58.7	Small 2016, 12, 13, 1709–1715		
Porous MoO <sub>2</sub> needs	1.49	54	Adv. Mater. 2016, 28, 3785–3790		
Co-B <sub>i</sub> NS/G hybrids	1.52	53	Angew. Chem. Int. Ed. 2016, 128,2534-2538		
LiCoO <sub>2</sub>	1.66	48	Energy Environ. Sci. 2016, 9, 184-192		
CoMnP	1.56	61	J. Am. Chem. Soc. 2016, 138, 4006–4009		
Ni–Co mixed oxide cages	1.61	50	Adv. Mater. 2016, 28, 4601–4605		

**Table S3** A comparison on OER catalytic data between our resultant catalysts and other reported non-precious metal based OER catalysts.



**Figure S16** (a) OER Polarization curves, (b) comparison of potentials recorded at 10 mA cm<sup>-2</sup>, (c) Tafel plots, and (d) EIS Nyquist plots of the  $Fe_{0.5}Co_{0.5}@NC/NCNS-800$  sample tested in both 0.1 M and 1.0 M KOH solutions.

#### **3.3 EIS plot fitting.**



**Figure S17** (a) Electric equivalent circuit (EEC) model used to explain the EIS response of OER on the investigated electrodes: two-time constant parallel model. (b) Fitting the OER EIS data of  $Fe_{0.5}Co_{0.5}@NC/NCNS-800$  recorded at 1.6 V vs. RHE by EEC shown in **Figure S17a**. Capacitance values (*C*) can be calculated by the equation proposed by Brug. et al (J. Electroanal. Chem. 1984, 176, 275-295.).

Electrochemical impedance spectroscopy (EIS) can permit us to know more information on the kinetics of the OER. Seeing from **Figure 3d** and **Figure S15d**, EIS data obtained on all as-developed control electrocatalysts can be characterized by two deformed semicircles in the complex plane plots; the first one appeared at high frequency range, and the second one appeared at low frequency range. Thus, a two-time constant parallel electric equivalent circuit (EEC) model can be used to explain the EIS response of different control samples (**Figure S17a**). For example, when we fitting the EIS data of  $Fe_{0.5}Co_{0.5}@NC/NCNS-800$  recorded at 1.6 V *vs*. RHE (**Figure S17b**), resistance of solution ( $R_s$ ) is fitted as about 6.52  $\Omega$ . The parameters obtained from the high frequency semicircle ( $C_1$ ,  $R_1$ ) are the typical responses for charge-transfer processes:  $C_1$  is the double layer capacitance of catalysts ( $C_{dl}$ ) and  $R_1$ is the charge transfer resistance ( $R_{ct}$ ). The  $R_{ct}$  value of  $Fe_{0.5}Co_{0.5}@NC/NCNS-800$ recorded for OER is 48.27  $\Omega$  at 1.6 V *vs*. RHE. Whereas, parameters obtained from the low frequency semicircle ( $C_2$ ,  $R_2$ ) are connected to adsorption processes on the electrode surface:  $C_2$  is the pseudo-capacitance ( $C_p$ ) and  $R_2$  is mass transfer resistance of the adsorbed intermediates ( $R_p$ ). The  $R_p$  value of Fe<sub>0.5</sub>Co<sub>0.5</sub>@NC/NCNS-800 recorded for OER is 26.33  $\Omega$  at 1.6 V vs. RHE. Similarly, all other EIS data for other control samples can be fitted by the same two-time constant parallel EEC model as shown in **Figure S17a**.

**3.4 OER** stability test.



**Figure S18** OER polarization plots of  $Fe_{0.5}Co_{0.5}@NC/NCNS-800$  catalyst before and after the OER accelerated degradation stability test in 1.0 M KOH (5000 CV cycles between 1.3-1.6 V *vs.* RHE).

### 4. HER electrocatalytic activity evaluation for resultant materials in

#### **1.0 M KOH solution.**

4.1 LSV curves, Tafel plots, and EIS Nyquist plots recorded for testing HER performances of different samples.



**Figure S19** (a) HER Polarization curves, (b) comparison of potentials recorded at 10 mA cm<sup>-2</sup>, (c) Tafel plots, and (d) EIS Nyquist plots recorded at -0.28 V for the  $Fe_{0.5}Co_{0.5}@NC/NCNS-T$  (T = 600, 700, 800, 900 and  $1000 \ ^{\circ}C$ ) catalysts.

Catalysts	$E_{10}$	Eonset	Tafel slop	References		
Fe <sub>4</sub> N@NC/NCNF-800	0.4522	0.33	65.3			
Fe <sub>0.7</sub> Co <sub>0.3</sub> @NC/NCNS-800	0.225	0.113	52.5			
Fe <sub>0.5</sub> Co <sub>0.5</sub> @NC/NCNS-800	0.15	0.063	49.1	This work		
Fe <sub>0.3</sub> Co <sub>0.7</sub> @NC/NCNS-800	0.183	0.088	51.6	I HIS WORK		
Co@NC/NCNS-800	0.219	0.109	55.8			
Pt/C	0.055	0.005	43.2			
Ni-NiO/N-rGO	0.26	-	67	Adv. Funct. Mater. 2015, 25, 5799-5808		
Ni <sub>2</sub> P	0.25	-	100	J. Am. Chem. Soc. 2013, 135(51): 19186		
Co <sub>0.6</sub> Mo <sub>1.4</sub> N <sub>2</sub>	0.32	-	80	Nat. Mater. 2012, 11(6): 550-557		
Co@CNF	0.196	-	96	Nano Energy 23 (2016) 105–113		
Zn <sub>0.30</sub> Co <sub>2.70</sub> S <sub>4</sub>	0.085	-	47.5-	J. Am. Chem. Soc. 2016, 138, 1359–1365		
EG/Co <sub>0.85</sub> Se/NiFe-LDH	0.26	0.24	160	Energy Environ. Sci., 2016, 9, 478-483		
Ni–B	0.135	-	88	Nano Energy (2016) 19, 98–107		
ONPPGC/OCC	0.446	-	154	Energy Environ. Sci., 2016, 9, 1210-121		
CoP/rGO-400	0.15	-	38	Chem. Sci., 2016, 7, 1690-1695		
Ni–Mo–N	0.043(20	-	40	Nano Energy (2016) 22, 111–119		
	mA cm <sup>-2</sup> )					
Porous MoO <sub>2</sub> Nanosheets	0.027	0	41	Adv. Mater. 2016, 28, 3785–3790		
Ni-NSAs in 0.1 M KOH	-	0.034	114	Angew. Chem. Int. Ed. 2016, 55,693 -697		
MoS <sub>2+x</sub> -CE	0.31	-	84	Angew. Chem. Int. Ed. 2015, 54, 664 -667		
CP/CTs/Co-S	0.19	-	131	ACS Nano 2016, 10, 2342-2348		
Ni <sub>5</sub> P <sub>4</sub>	0.15	<-0.1	53	Angew. Chem. Int. Ed. 2015, 127,12538		
NI: C - /NIE	0.096		120	Angew. Chem. Int. Ed. 2015, 54,9351		
INISE/INF		-		-9355		
NiFeO <sub>x</sub> /CFP	0.088	-0.04	84.6	Nature Communications 2015, 6, 7261		

**Table S4** Comparison of HER activity data for those resultant catalysts and other reportednon-precious metal based HER catalysts.

4.2 Comparation of HER LSV curves and Tafel plots for  $Fe_{0.5}Co_{0.5}@NC/NCNS-800$  recorded in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 1.0 M KOH solutions.



**Figure S20** (a) HER Polarization curves and (b) Tafel plots of  $Fe_{0.5}Co_{0.5}@NC/NCNS-800$  recorded in 0.5 M H<sub>2</sub>SO<sub>4</sub> (black lines) and 1 M KOH solutions (red lines).

The HER catalytic activity of  $Fe_{0.5}Co_{0.5}@NC/NCNS-800$  was also evaluated in 0.5 M H<sub>2</sub>SO<sub>4</sub>, nevertheless, the catalytic performances recorded in acid (including both  $E_{onset}$  and  $E_{10}$ ) are much worse than those got in alkaline solution (**Figure S20a**). A Tafel slope of approximately 133.2 mV dec<sup>-1</sup> in acidic solution is much larger than that of 49.1 mV dec<sup>-1</sup> in alkaline solution, indicating that the Volmer step is the rate-determining step for HER in acidic solution (**Figure S20b**).

#### 4.3 EIS Nyquist plots fitting.



**Figure S21** (a) Electric equivalent circuit (EEC) model used to analyze the EIS data of HER on investigated electrodes: two-time constant parallel model. (b) Fitting the HER EIS data of  $Fe_{0.5}Co_{0.5}@NC/NCNS-800$  recorded at -0.28 V *vs*. RHE by EEC shown in **Figure S21a**. Double layer capacitances (c) can be calculated by the equation proposed by Brug. et al (J. Electroanal. Chem.1984,176, 275-295.).

Similar to that of OER, EIS can also permit us to know more information on the kinetics of the HER. Seeing from **Figure 4d** and **Figure S19d**, EIS data obtained on all as-developed control electrocatalysts for HER can also be characterized by two deformed semicircles in the complex plane plots; the first one appeared at high frequency range, and the second one appeared at low frequency range. Thus, a two-time constant parallel electric equivalent circuit (EEC) model was used to explain the EIS response of different control samples (**Figure S21a**). For example, when we fitting the EIS data of Fe<sub>0.5</sub>Co<sub>0.5</sub>@NC/NCNS-800 recorded at -0.28 V *vs*. RHE (as shown in **Figure S21b**), resistance of solution ( $R_s$ ) is fitted to about 5.34  $\Omega$ . The parameters obtained from high frequency semicircle are also the typical responses for charge-transfer processes in HER:  $R_{ct}$  of Fe<sub>0.5</sub>Co<sub>0.5</sub>@NC/NCNS-800 recorded at -0.28 V *vs*. RHE for HER is 12.32  $\Omega$ . Whereas, parameters obtained from the low

frequency semicircle are connected to the adsorption processes of the adsorbed intermediates on electrode surfaces:  $R_p$  of Fe<sub>0.5</sub>Co<sub>0.5</sub>@NC/NCNS-800 recorded at -0.28 V *vs.* RHE for HER is 36.98  $\Omega$ . As the similar tendencies of EIS plots for all control samples, each sample can be fitted by the same two-time constant parallel EEC model shown in **Figure S21a**.

4.4 HER stability test.



**Figure S22** LSV curves of  $Fe_{0.5}Co_{0.5}@NC/NCNS-800$  for HER recorded in 1.0 M KOH before and after  $5000^{th}$  CV cycles between -0.2-0.1 V vs. RHE.

#### 4.5 The measurement of Tafel slopes by EIS.

When fitting a Tafel slope, it is subjective for the choice of the regions on the current voltage curves whether the *iR*-drops are corrected by different ways in which or not. Meantime, the apparent Tafel slope extracted from the polarization curve will be higher than the true value, if electron transport in the catalyst is sufficiently slow. From the two perspectives, those Tafel slopes based on polarisation curves are not very accurate with regard to measuring the precise HER mechanism at each catalyst. Therefore, in order to clearly elucidate that  $Fe_{0.5}Co_{0.5}@NC/NCNS-800$  is a highly active catalyst, there is a necessary to develop a new technique that goes beyond a less efficient Tafel analysis related to HER polarisation curves. Recently, EIS-based

analysis of Tafel slopes has been demonstrated as an efficient method for overcoming the above disadvantages.



**Figure S23** Nyquist plots recorded at various HER overpotentials in 1.0 M KOH (insert represent high frequency region) for Fe<sub>4</sub>N@NC/NCNF-800 (**a**), Fe<sub>0.7</sub>Co<sub>0.3</sub>@NC/NCNS-800 (**b**), Fe<sub>0.3</sub>Co<sub>0.7</sub>@NC/NCNS-800 (**c**), and Co@NC/NCNS-800 (**d**). Tafel slopes fitted from EIS data measured in the *E*-log ( $1/R_{ct}$ ) plots for Fe<sub>4</sub>N@NC/NCNF-800 (**a**'), Fe<sub>0.7</sub>Co<sub>0.3</sub>@NC/NCNS-800 (**b**'), Fe<sub>0.3</sub>Co<sub>0.7</sub>@NC/NCNS-800 (**c**'), and Co@NC/NCNS-800 (**d**').

A two-time constant parallel EES model shown in **Figure S21** is used to explain the EIS response of the HER. As can be seen in **Figures 5a-b and Figure S23**,  $Fe_{0.5}Co_{0.5}@NC/NCNS-800$  still displays the minimum EIS-based Tafel slope compared with other reference samples. Its Tafel slope of 46.7 mV decade<sup>-1</sup> is between 38 and 116 mV dec.<sup>-1</sup>, which suggests that a Volmer-Heyrovsky mechanism is responsible for the HER process of  $Fe_{0.5}Co_{0.5}@NC/NCNS-800$ ; meantime, the rates of both discharge and desorption steps are comparable during the HER process. On the other hand, the Tafel slope fitted from polarization curve (49.1 mV dec<sup>-1</sup>) is only a little larger than that obtained from  $R_{ct}$  values (46.7 mV dec<sup>-1</sup>), suggesting that electron transport resistance cannot be comparable to charge transfer resistance for the  $Fe_{0.5}Co_{0.5}@NC/NCNS-800$  at the catalyst/electrolyte interface. This result also proves the high electron transport rate of each  $Fe_{0.5}Co_{0.5}@NC/NCNS$  nanosheest.

**Table S5** EEC parameters obtained by fitting EIS experimental spectra for $Fe_{0.5}Co_{0.5}@NC/NCNS-800$  recorded at various overpotentials and for different samples recordedat -0.3 V vs. RHE in 1 M KOH solution. The two-time constant parallel EEC model shown in**Figure S21** is used to fit the EIS parameters of the HER on the investigated electrodes.

Samples	E / V vs. RHE	$R_s/\Omega$ cm <sup>2</sup>	$R_{ct}/\Omega$ $cm^2$	$\frac{Q_1/m\Omega}{cm^{-2}}$	n <sub>1</sub>	C <sub>dl</sub> /mF cm <sup>-2</sup>	$R_{P}/\Omega$ $cm^{2}$	$\frac{Q_{P}/m\Omega}{^{-1} \text{ cm}^{-2}}$	n <sub>P</sub>	C <sub>P</sub> /F cm <sup>-2</sup>
	-0.21	5.422	25.48	9.10	0.450	4048.4 2	92.55	5.90	0.972	1.400
	-0.22	5.459	21.51	8.40	0.459	1867.4 7	78.51	5.80	0.932	1.997
	-0.23	5.265	20.41	8.17	0.465	1428.4 2	58.34	5.48	0.971	1.399
Fe <sub>0.5</sub> Co <sub>0.5</sub> @NC/NCNS-8	-0.24	5.416	14.61	5.66	0.499	319.49	45.91	5.32	0.883	2.803
00	-0.26	5.349	13.08	4.50	0.521	35.23	41.19	5.14	0.857	3.307
	-0.28	5.338	12.32	4.25	0.526	28.12	36.98	5.1	0.846	3.574
	-0.30	5.398	10.97	3.58	0.544	14.99	35.1	5.12	0.814	4.525
	-0.32	5.483	10.11	2.81	0.565	7.59	26.01	4.81	0.798	4.689
	-0.34	5.575	7.95	2.11	0.598	4.19	24.81	4.94	0.733	7.774
	-0.36	5.515	7.54	1.78	0.614	3.22	20.42	4.97	0.711	9.546
	-0.40	5.649	6.538	1.5	0.631	2.61	19.02	4.78	0.652	13.53
Fe <sub>4</sub> N@NC/NCNF-800		6.328	40.03	4.6	0.55	23.73	508.7	4.41	0.873	1.293
Fe <sub>0.7</sub> Co <sub>0.3</sub> @NC/NCNS-8 00	-0.30	6.878	12.72	3.5	0.43	28.29	110.8	2.53	0.747	2.495
Fe <sub>0.5</sub> Co <sub>0.5</sub> @NC/NCNS-8 00		5.398	10.97	3.58	0.544	14.99	35.1	5.12	0.814	4.525
Fe <sub>0.3</sub> Co <sub>0.7</sub> @NC/NCNS-8 00		5.848	11.52	6.27	0.48	234.39	98.7	2.66	0.884	2.817
Co@NC/NCNS-800		5.486	12.35	0.425	0.64	1.29	461.4	1.03	0.836	2.293

**4.6 CV curves recorded at different scan rates for estimating the electrochemical active area.** 



**Figure S24** CV curves recorded at different scan rates from 5 to 50 mV s<sup>-1</sup> (inset are the amplification views of CVs between 0.85-0.95 V *vs.* RHE) for Fe<sub>4</sub>N@NC/NCNF-800 (**a**), Fe<sub>0.7</sub>Co<sub>0.3</sub>@NC/NCNS-800 (**b**), Fe<sub>0.3</sub>Co<sub>0.7</sub>@NC/NCNS-800 (**c**), and Co@NC/NCNS-800 (**d**).

4.7 Gas evolution measurements for Fe<sub>0.5</sub>Co<sub>0.5</sub>@NC/NCNS-800



**Figure S25** The theoretically calculated and experimentally measured gas amounts *versus* time for the overall water splitting of  $Fe_{0.5}Co_{0.5}@NC/NCNS-800$ .

# 5. Insighting into the excellent OER and HER catalytic ability of Fe<sub>0.5</sub>Co<sub>0.5</sub>@NC/NCNS-800.

5.1 Insighting into the roles of NCNSs, FeCo cores, and NC shells of  $Fe_{0.5}Co_{0.5}@NC/NCNS-800$  in OER/HER catalysis.



**Figure S26** TEM image of acid-Fe<sub>0.5</sub>Co<sub>0.5</sub>@NC/NCNS-800 sample after 10 h of acid treatment in the 5.0 M mixture acid solution of  $H_2SO_4$  and HCl (1: 1).

Finally, as  $Fe_{0.5}Co_{0.5}@NC/NCNS$  shows good activities and stabilities in both OER and HER processes. We wish to explore the role of each content in boosting OER/HER catalysis abilities. As shown in **Figure S26**, upon the as-synthesized  $Fe_{0.5}Co_{0.5}@NC/NCNS-800$  sample suffered from 10 h of reflux reaction in 5.0 M mixture acid solution of H<sub>2</sub>SO<sub>4</sub> and HCl (1: 1), the resultant sample (denoted as acid-Fe\_{0.5}Co\_{0.5}@NC/NCNS-800) shows entirely different morphology and structure compared with that for  $Fe_{0.5}Co_{0.5}@NC/NCNS-800$ . It is clear that large amounts of  $Fe_{0.5}Co_{0.5}@NC$  units are still existed; meantime, most  $Fe_{0.5}Co_{0.5}$  alloy cores of the  $Fe_{0.5}Co_{0.5}@NC$  units were corroded and dissolved, but the outer carbon shells can be observed obviously. These results also demonstrate the  $Fe_{0.5}Co_{0.5}$  alloy cores are indeed embedded into the carbon shells.



**Figure S27** (a) OER LSV curves and (b) HER LSV curves of acid-Fe<sub>0.5</sub>Co<sub>0.5</sub>@NC/NCNS-800, Fe<sub>0.5</sub>Co<sub>0.5</sub>@NC/NCNS-800, Fe<sub>0.5</sub>Co<sub>0.5</sub>@NC, and pure Fe<sub>0.5</sub>Co<sub>0.5</sub> sample recorded in 1.0 M KOH.

5.2 Insighting into the reason why the  $Fe_{0.5}Co_{0.5}@NC/NCNS-800$  shows high OER catalytic activity along with an excellent stability by SEM, TEM, and XPS characterizations.



**Figure S28** SEM (a) and TEM (b) images of  $Fe_{0.5}Co_{0.5}@NC/NCNS-800$  material after the OER accelerated degradation stability test in 1 M KOH (5000 CV cycles between 1.3-1.6 V vs. RHE).



**Figure S29** Comparation of high-resolution C 1s (**a**), O 1s (**b**), N 1s (**c**), Fe 2p (**d**), Co 2p (**e**) XPS spectra for  $Fe_{0.5}Co_{0.5}@NC/NCNS-800$  sample before and after OER stability test in 1.0 M KOH.

Besides high OER catalytic activity, the  $Fe_{0.5}Co_{0.5}@NC/NCNS-800$  also features excellent stability, as revealed by a typical accelerated degradation test for 5000 continuous CV cycles (**Figure S18**). The  $Fe_{0.5}Co_{0.5}@NC/NCNS-800$  catalyst only shows a slight decay with an overpotential increase of 8 mV for achieving 20 mA cm<sup>-2</sup>, suggesting its superior durability.

The SEM image (**Figure S28a**) of the post-OER  $Fe_{0.5}Co_{0.5}$ @NC/NCNS-800 catalyst indicates that the 3D hierarchical porous channels are completely kept after OER catalysis, which will throughout afford enough channels for mass/electron transmission relating to OER. On the other hand, various mesopores scattering on the surfaces of each carbon nanosheet have also been perfectly remained for the post-OER  $Fe_{0.5}Co_{0.5}$ @NC/NCNS-800 as can be seen in its TEM image (**Figure S28b**). It can be seen that changes in both morphology and structure are negligible for  $Fe_{0.5}Co_{0.5}$ @NC/NCNS-800 after the accelerated degradation test; its 3D hierarchical meso/macroporous architectures are quite stable. Meanwhile, both structures of the outer graphitic carbon layers and the encapsulating FeCo alloy cores are still well

maintained after the OER durability measurements (5000 CV sweeps), as confirmed by typical HRTEM analysis shown in Figure S28b, revealing the excellent stability of the well dispersive and electroactive FeCo@NC units in 1.0 M KOH. In order to gain further insights into its nature towards the OER, XPS measurements of Fe<sub>0.5</sub>Co<sub>0.5</sub>@NC/NCNS-800 system before and after OER tests are employed to probe their surface compositions and chemical states. Obvious increase in peak intensity of C-O and O-C=O species is observed in the C 1s (Figure S29a) and O 1s (Figure S29b) XPS spectra of the post-OER Fe<sub>0.5</sub>Co<sub>0.5</sub>@NC/NCNS-800 respectively. These functional groups present on each carbon nanosheet can be ionized into C-O<sup>-</sup>/-COO<sup>-</sup> and simultaneously render adjacent carbon atoms positively charged because of the electron with drawing oxygen atoms in a typical  $\pi$ -system. These oxygen-containing groups might be additional active sites to expedite oxygen evolution. Abundant edges and defective sites dispersed along the 3D hierarchical meso/macroporous structures could interact with N atoms to form C-N bonds in the N doping process, which can also render the adjacent carbon atoms positively charged (act as the OER catalytic active sites). Meanwhile, the intensity of C-N bonds displays a tiny decay for post-OER Fe<sub>0.5</sub>Co<sub>0.5</sub>@NC/NCNS-800 (Figure S29a). Indeed, except for the pyrrolic N, both pyridinic N and graphitic N are really stable in the OER catalysis processes; thus, the decrease of C-N species is mainly ascribed to the decomposition of pyrrolic N (Figure S29c). The Fe 2p<sub>3/2</sub> spectrum of post-OER Fe<sub>0.5</sub>Co<sub>0.5</sub>@NC/NCNS-800 still displays peaks for metallic Fe and Fe(II/III) respectively, whereas metallic Fe decrease accompanying the increase of Fe(II/III) (Figure S29d). Seeing from the Co 2p<sub>3/2</sub> spectrum of post-OER Fe<sub>0.5</sub>Co<sub>0.5</sub>@NC/NCNS-800 (Figure S29e), one can observe that metallic Co and Co-N are stable with partial Co (II) has transformed into the Co (III). Even so, we can see from O 1s spectrum that no obvious rise of M-O species on the surfaces appears for post-OER Fe0.5Co0.5@NC/NCNS-800 (Figure **S29b**). All these results demonstrate that the transformation between metallic Fe/Co and Fe(II/III)/Co(II/III) as electron have transferred from the encapsulated FeCo alloy NPs to the outer graphitic carbon layers rather than the appearing of new metal oxides. In other word, the outer carbon shells perfectly prevent the oxidizing of FeCo cores

and FeCo cores significantly alter the electronic properties of outer graphitic carbon shells. This interaction further tunes the binding energies of reaction intermediates for promoting OER process. In addition, as shown in **Figure 29c and Figure 29e**, those electroactive M-N species are also stable. Taken together, it indicated that the 3D hierarchically meso/macroporous structures and the electroactive FeCo@NCs units are quite stable during OER. Along with the abundant OER active C-O<sup>-</sup>, -COO<sup>-</sup>, C-N, and M-N species, the conception new Fe<sub>0.5</sub>Co<sub>0.5</sub>@NC/NCNS-800 catalyst displays the ultra-high OER electrocatalytic activity, which even surpasses the commercially available RuO<sub>2</sub>. In addition, the slight decay in current density of post-OER Fe<sub>0.5</sub>Co<sub>0.5</sub>@NC/NCNS-800 is mainly caused by the decomposition of a little unstable pyrrolic N species.

5.3 Insighting into the reason why the  $Fe_{0.5}Co_{0.5}@NC/NCNS-800$  shows high HER catalytic activity along with an excellent stability by SEM, TEM, and XPS characterizations.



**Figure S30** SEM (a) and TEM (b) images of post-HER  $Fe_{0.5}Co_{0.5}@NC/NCNS-800$  after the HER accelerated degradation stability test in 1.0 M KOH (5000 CV cycles between 1.3-1.6 V vs. RHE).

Besides high HER catalytic activity, the  $Fe_{0.5}Co_{0.5}@NC/NCNS-800$  also features excellent stability, as revealed by a typical accelerated degradation test for 5000 continuous CV cycles (**Figure S22**). The  $Fe_{0.5}Co_{0.5}@NC/NCNS-800$  catalyst only shows a slight decay.

The SEM image (**Figure S30a**) of the post-HER  $Fe_{0.5}Co_{0.5}@NC/NCNS-800$  reveals that the 3D hierarchical porous channels have been completely kept after HER catalysis, which will enhance the mass/electron transmission rates relating to HER. At

the same time, various mesopores dispersing on the surfaces of all carbon nanosheets can also been found obviously for the post-HER Fe0.5Co0.5@NC/NCNS-800 from its TEM image (Figure S30b). As can be seen that the changes in both morphology and structure are negligible for post-HER Fe<sub>0.5</sub>Co<sub>0.5</sub>@NC/NCNS-800 after the accelerated degradation test; its 3D hierarchical meso/macroporous architectures are quite stable. Meanwhile, structures of the outer graphitic carbon shells and the encapsulating FeCo alloy cores are fairly stable in the HER catalysis, as exposed by the typical HRTEM (Figure S30b), demonstrating the excellent stability of the well dispersed FeCo@NC units. In order to gain further insights into its high efficiency nature to HER, XPS of Fe0.5Co0.5@NC/NCNS-800 measurements initial and post-HER Fe<sub>0.5</sub>Co<sub>0.5</sub>@NC/NCNS-800 systems before and after HER tests are employed to probe their surface compositions and chemical states. Negligible changes in peak intensity of C-O and O-C=O species can be observed in the C 1s (Figure S31a) and O 1s (Figure S31b) XPS spectra of the post-HER Fe<sub>0.5</sub>Co<sub>0.5</sub>@NC/NCNS-800 respectively. However, an obvious decay in peak intensity of C-O-C and C-OH species is visual in O 1s (Figure S31b) XPS spectra. Abundant edges and defective sites dispersed along the 3D hierarchical meso/macroporous structures could interact with N atoms to form C-N bonds in the N doping process, which can act as the HER catalytic active sites. Meantime, as the surface activation, the intensity of C-N bonds shows a tiny increase for post-HER Fe<sub>0.5</sub>Co<sub>0.5</sub>@NC/NCNS-800 (Figure S31a). Indeed, except for the pyrrolic N, both pyridinic N and graphitic N are really stable in the HER catalytic processes; furthermore, an increase of pyridinic N-M species can be clearly observed in N 1s spectrum (Figure S31c). The Fe  $2p_{3/2}$  and Co  $2p_{3/2}$  spectra of post-HER Fe<sub>0.5</sub>Co<sub>0.5</sub>@NC/NCNS-800 still displays peaks for metallic Fe/Co and Fe(II/III)/Co(II/III) respectively for post-HER Fe<sub>0.5</sub>Co<sub>0.5</sub>@NC/NCNS-800, but the contents of them changes slightly (Figures S31d-e). This phenomenon demonstrates that electron interchange between the encapsulated FeCo alloy cores and the outer graphitic carbon layers but no new metal oxide appears (as shown in Figure S31b, intensity of M-O shows no change in the O 1s spectrum). In other word, the outer carbon shells perfectly prevent the oxidizing of FeCo cores and FeCo cores significantly alter the electronic properties of outer graphitic carbon shells. This interaction further tunes the binding energies of reaction intermediates for promoting HER process. XPS results of the post-HER catalyst also indicate the partial reduction of the Co (II/III) as less amounts of Co (II/III) species appear after the HER (**Figure S31e**).



**Figure S31** Comparation of High-resolution C 1s (a), O 1s (b), N 1s (c), Fe 2p (d), Co 2p (e) XPS spectra for  $Fe_{0.5}Co_{0.5}@NC/NCNS-800$  before and after HER stability test in 1 M KOH.