### **Supporting information**

## CoP/N-doped carbon hollow spheres anchored on electrospinning core-shell N-doped carbon nanofibers as efficient electrocatalysts for water splitting

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Containing: 27 pages, 17 Figures and 4 Tables

Experimental detail, additional images and data:

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**Figure. S12** (a) CV curves of the catalysts in 1.0 M PBS (pH=7) with scan rate of 50

 $mV \cdot s^{-1}$ . Calculated TOF of the catalysts for HER in (b) 0.5 M H<sub>2</sub>SO<sub>4</sub> and (c) 1.0 M KOH, and for OER in (d) 1.0 M KOH.

**Figure. S13** CV curves of (a) CoP/NCF-100, (b) CoP/NCF-300, (c) CoP/NC and (d) NCF at different scan rates from 5 to 25 mV $\cdot$ s<sup>-1</sup> at the potential window of 0.054-0.150 V (vs. RHE) in 1.0 M KOH.

**Figure. S14** The theoretical models of H\* adsorbed on: (a) Graphene, (b) N-Graphene, (c) CoP, (d) CoP/Graphene and (e) CoP/N-Graphene. The grey, green, blue, violet and white balls represent C, N, Co, P and H atoms, respectively.

**Figure. S15** CV curves of (a) CoP/NCF-100, (b) CoP/NCF-300, (c) CoP/NC and (d) NCF at different scan rates from 5 to 25 mV·s<sup>-1</sup> at the potential window of 1.4-1.5 V (vs. RHE) in 1.0 M KOH.

**Figure S16** High resolution (a) Co 2p and (b) P 2p XPS spectra of the CoP/NCF-200 before and after 10 h stability test for OER.

Figure. S17 The XRD spectra of CoP/NCF-200 after 10 h stability test for OER.

Table S1 Summary of various non-noble metal catalysts for HER in 0.5 M H<sub>2</sub>SO<sub>4</sub>.

Table S2 Summary of various non-noble metal catalysts for HER in 1 M KOH.

**Table S3** Summary of various non-noble metal catalysts for OER in 1.0 M KOH.**Table S4** Summary of various catalyts for overall water splitting in 1.0 M KOH.

#### 1. Materials and reagents

Cobalt (II) nitrate hexahydrate,  $RuO_2$  were purchased from Aladdin chemical reagent company. Pt/C (20 wt% Pt on carbon black) and Nafion (5 wt%) were supplied by Alfa Aesar. All reagents were of analytical grade and were used as received.

#### 2. Catalyst characterization

Scan electron microscope (SEM) images were collected using a field-emission scanning electron microscope (JSM-6701F, FEOL). Transmission electron microscopy (TEM) images were taken with a JEM-2010 transmission electron microscope. High resolution-transmission electron microscopy (HR-TEM) images were collected on Tecnai G2 F30 Field Emission Transmission Electron Microscope. The X-ray power diffraction (XRD) patterns of the samples were obtained on a Shimadzu XRD-6000 diffractometer with Cu K $\alpha$  radiation ( $\lambda$ =1.54178 Å). Atomic absorption results were obtained on a Hitachi 180-80 polarized Zeeman atomic absorption spectrophotometer. The nitrogen adsorption-desorption characterization were performed with an ASAP2020 Micromeritics instrument at 77 K. The SL200 KB apparatus was used to measure the contact angles (CAs). The X-ray photoelectron spectroscopy (XPS) was obtained at a Thermo Fisher Scientific's K-Alpha X-ray photoelectron spectrometer.

#### 3. Electrochemical measurements

#### **3.1 For HER and OER**

The electrocatalytic performances of the catalysts were tested on a CHI 760E electrochemical workstation equipped with a three-electrode system. A 3 mm glassy carbon (GC), a graphite rod and a Ag/AgCl (in 3M KCl) electrode was used as

working electrode, counter electrode and reference electrode, respectively. All catalyst inks were prepared by ultrasonically dispersing 5.0 mg of catalyst into 0.5 mL ethanol containing 10  $\mu$ L 5 wt% Nafion. The working electrode was prepared by depositing above suspension on the well polished working electrode and the electrode was dried at room temperature. The catalyst loading was 0.23 mg cm<sup>-2</sup> for the electrochemical tests. For comparison purpose, electrocatalytic activity of commercial Pt/C (20%) and RuO<sub>2</sub> were evaluated under the same conditions with the identical catalyst loading. Electrochemical impedance spectroscopy (EIS) was measured with amplitude of 5 mV in a frequency range of 10<sup>-1</sup>-10<sup>6</sup> Hz. All the electrochemical tests were conducted at room temperature after the catalyst was stabilized by CV, and the potentials were calibrated to reversible hydrogen electrode (RHE) based on the equation of E(RHE) = E (Ag/AgCl) + 0.0591 pH +0.197 V.

#### 3.2 Overall water splitting test

Typically, 10.0 mg CoP/NCF-200 sample was dispersed in a water/ethanol solution (1.0 mL, 3:1 V/V) with 50  $\mu$ L Nafion solution (5%) by ultrasound for 1 h to form a homogeneous ink. Then, 80  $\mu$ L of the ink was dropped on a Ni foam (1x1 cm) and left to dry in a vacuum oven at room temperature (catalyst loading on Ni foam was 0.80 mg cm<sup>-2</sup>).

#### 3.3 Turnover frequency (TOF) calculation

The turnover frequency (TOF,  $s^{-1}$ ) for HER was calculated with the following equation:

$$\text{TOF} = \frac{|J| \cdot A}{2F \cdot n} \quad (S1)$$

The TOF for OER was calculated with the following equation:

$$\mathrm{TOF} = \frac{|J| \cdot A}{4F \cdot n} \quad (\mathbf{S2})$$

Where |J| (A cm<sup>-2</sup>) is the current density at a fixed voltage during the LSV measurement, A is the geometric area of the working glassy carbon electrode (0.07 cm<sup>2</sup>), F is the Faraday constant (96485 C mol<sup>-1</sup>), and n is the number of active sites

(mol). The factor of 2 or 4 is the corresponding electron transfer numbers.

The number of active sites (*n*) was estimated by using the methods reported previously. <sup>1-5</sup> The catalyst was first examined employing cyclic voltammogram in 1.0 M PBS solution with the potential range of -0.2 to 0.6 V (vs. RHE) at a scan rate of 50 mV s<sup>-1</sup> (**Figure S12a**). The number of active sites *n* is proportional to the charge *Q*, which can be calculated from the obtained CV curve by integrating. Therefore, active sites could be obtained from the following equation:

$$n = \frac{Q}{2F} = \frac{I \cdot t}{2F} = \frac{I \cdot V/u}{2F} = \frac{S}{2F \cdot u} \quad (S3)$$

Where *S* is integrated effective area in CV recorded, *I* is the current (A), *V* is the voltage (V), *u* is the scan rate (50 mV s<sup>-1</sup>).

#### 3.4 Determining of Electrochemical active surface area (ECSA)

Electrochemical capacitance measurements were used to determine the active surface area of catalyst. To measure the electrochemical capacitance, CV curves with various scan rates (5, 10, 15, 20 and 25 mV s<sup>-1</sup>) were measured in non-Faradic potential window. By plotting the capacitive currents ( $\Delta J=J_{anodic}-J_{cathodic}$ ) against the scanning rate at the central voltage and following with a linear fit, the double layer capacitance ( $C_{dl}$ ) can be estimated as half of the slope. From the double layer capacitance ( $C_{dl}$ ) and capacitance of an atomically smooth planar surface ( $C_s$ ), the ECSA was calculated using the following equation:

$$ECSA = \frac{c_{dl}}{c_s} \quad (S4)$$

Where  $C_s$  is the specific capacitance for a flat surface, which was generally found to be in the range of 20-60  $\mu$ F cm<sup>-2</sup>. In the following calculations, we assumed 40  $\mu$ F cm<sup>-2</sup> for  $C_s$  according to previous reports.<sup>6-11</sup>

#### **3.5** The exchange current density $(j_0)$

The Tafel slope was calculated according to Tafel equation as follows:

 $\eta = b\log/j/ + a$ , where  $\eta$  is overpotential (V), *j* is current density (mA cm<sup>-2</sup>), and *b* is the Tafel slope (mV dec<sup>-1</sup>). The exchange current density can be obtained by extrapolating the Tafel curve to zero overpotential (exchange current density *j*=*j*<sub>0</sub> at

# η=0 V).**3.6 The Faradaic efficiency** (*FE*)

The Faradaic efficiency was calculated by comparing the experimentally produced gas volume with the theoretically calculated one:

$$FE = V_{experimental}/V_{theoretical}$$
 (S5)

The experiment volumes of  $H_2$  or  $O_2$  were measured by drainage. The theoretical volume can be calculated using the formula:

$$V_{theoretical} = I \cdot t \cdot V_m / n \cdot F \qquad (S6)$$

Where *I* is the electrolysis current, *t* is the electrolysis time,  $V_m$  is molar volume of H<sub>2</sub>/O<sub>2</sub> of gas (24.5 L mol<sup>-1</sup>, 298 K, 101 kPa),<sup>12</sup> *n* is the number of electrons required for one molecule of H<sub>2</sub> or O<sub>2</sub> and *F* is the Faraday's constant (96485 C/mol).

#### 4. Density function theory (DFT) calculation

In this work, the density functional theory (DFT) calculations were performed using the Dmol<sup>3</sup> code.<sup>13</sup> The exchange-correlation interaction was treated by the generalized gradient approximation (GGA) with PBE functional.<sup>14</sup> A double numerical quality basis set with d-type polarization function (DNP<sup>3</sup>) was utilized for all the geometric optimizations, total energy calculations.<sup>15</sup> Grimme's semi-empirical DFT-D was introduced in the computations to guarantee a better description of the electron interaction in a long range.<sup>16</sup> The core electrons were modeled using effective core pseudopotentials (ECP) by Dolg<sup>17</sup> and Bergner.<sup>18</sup> All calculations were spin unrestricted. The positions of all the atoms were fully relaxed until the following convergence criterion are met respectively: 0.002 Ha/Å for force,  $10^{-5}$  Ha for total energy and 0.005 Å for displacement. The real space cutoff radius was 4.1 Å. The self-consistent field (SCF) computations criterion was chosen to be  $10^{-6}$  Ha on the total energy to achieve accurate electronic convergence.  $3 \times 3 \times 1$  Monkhorst-Pack grid k-points were employed for geometric optimization.

In present work, ZIF-67 derived graphitic N-doped carbon layers can be ideally

regarded as a single layer of graphene for convenient calculations.<sup>19</sup> **Figure S14** shows the theoretical model for graphene (Graphene), nitrogen-doped graphene (N-Graphene), CoP covered by nitrogen-doped graphene (CoP/N-Graphene), as well as the composited CoP covered by graphene (CoP/Graphene) and sole CoP systems for comparative purpose. Specifically, the CoP (011) surface is modeled and the lattice parameters of CoP are 5.599 Å, 5.176 Å, 3.281 Å. In order to simplify the computation for comparison of qualitative merely, we have sampled the nitrogen-doped graphene layer with the N/C atomic ratio of 1:17. The top three layers of CoP (011) and graphene were allowed to relax, while the rest of CoP (011) (the bottom three layers) remained fixed.



**Figure S1** Optical images of the (a) PAN nanofibers, (b) PAN@PPy, (c) ZIF-67 powders and (d) PAN@PPy-ZIF-67.



**Figure S2** XRD patterns of Simulated ZIF-67, As-synthesized ZIF-67 and PAN@PPy-ZIF-67 samples.



**Figure S3** SEM images of (a-b) PAN nanofibers; (c-d) PAN@PPy and (e-f) PAN@PPy-ZIF-67.



**Figure S4** The full survey XPS spectrum of (a) CoP/NCF-100, (b) CoP/NCF-300, (c) CoP/NC and (d) NCF.



**Figure S5** High resolution C1s XPS spectrum of (a) CoP/NCF-100, (b) CoP/NCF-300, (c) CoP/NC and (d) NCF.



**Figure S6** High resolution N1s XPS spectrum of (a) CoP/NCF-100, (b) CoP/NCF-300, (c) CoP/NC and (d) NCF.



**Figure S7** High resolution O1s XPS spectrum of (a) CoP/NCF-100, (b) CoP/NCF-300, (c) CoP/NC and (d) NCF.



**Figure S8** High resolution P2p XPS spectrum of (a) CoP/NCF-100, (b) CoP/NCF-300 and (c) CoP/NC.



**Figure S9** High resolution Co2p XPS spectrum of (a) CoP/NCF-100, (b) CoP/NCF-300 and (c) CoP/NC.



**Figure S10** Wettability test of (a) CoP/NCF-100 and (b) CoP/NCF-300. The image at 0 s was captured when the water droplet rests on the surface.

Sample	Overpotential @j=10mA cm <sup>-2</sup> (mV)	Tafel slope (mV dec <sup>-1</sup> )	Reference
CoP/CNT <sup>a</sup>	122	54	Angew. Chem. Int. Ed. <b>2014</b> , <i>53</i> (26), 6710-6714
Cu <sub>3</sub> P NW/CF <sup>b</sup>	143	67	Angew.Chem. Int. Ed. <b>2014</b> , <i>53</i> (36), 9577-9581
MoP/CF <sup>c</sup>	200	56.4	Appl. Catal., B 2015, 164, 144-150
Co <sub>2</sub> P@NPG <sup>d</sup>	103	58	Nano Lett . 2016, 16 (7), 4691-4698
CoP-CNTs <sup>e</sup>	139	52	Small <b>2017</b> , <i>13</i> (5), 1602873
Fe/P/C <sub>0.5</sub> -800 <sup>f</sup>	256	53.6	Nano Energy. 2017, 33, 221-228
N/Co-doped PCP/NRGO <sup>g</sup>	229	126	Adv. Funct. Mater. <b>2015</b> , <i>25</i> (6), 872-882
CoP/CNF-200	86	55	This work

Table S1 Summary of various non-noble metal catalysts for HER in 0.5 M H<sub>2</sub>SO<sub>4</sub>.

<sup>a</sup> Carbon nanotubes decorated with CoP nanocrystals (CoP/CNT);

<sup>b</sup> Self-supported Cu<sub>3</sub>P nanowire arrays on commercial porous copper foam;

<sup>c</sup> MoP nanosheets supported on biomass-derived carbon flake;

<sup>d</sup> Dicobalt phosphide (Co<sub>2</sub>P) nanoparticles encapsulated in N,P-doped graphene;

<sup>e</sup> The hybrid of CoP/carbon nanotubes;

<sup>f</sup>Three-dimensional (3D) hybrid carbon composite (Fe/P/C nanowire networks);

<sup>g</sup>Cobalt and nitrogen codoped graphene with inserted carbon nanospheres.



Figure S11 CV curves of (a) CoP/NCF-100, (b) CoP/NCF-300, (c) CoP/NC and (d) NCF at different scan rates from 5 to 25 mV·s<sup>-1</sup> at the potential window of 0.02-0.12 V (vs. RHE) in 0.5 M H<sub>2</sub>SO<sub>4</sub>.



**Figure S12** (a) CV curves of the catalysts in 1.0 M PBS (pH=7) with scan rate of 50  $\text{mV}\cdot\text{s}^{-1}$ . Calculated TOF of the catalysts for HER in (b) 0.5 M H<sub>2</sub>SO<sub>4</sub> and (c) 1.0 M KOH, and for OER in 1.0 M KOH (d).



Figure S13 CV curves of (a) CoP/NCF-100, (b) CoP/NCF-300, (c) CoP/NC and (d) NCF at different scan rates from 5 to 25 mV $\cdot$ s<sup>-1</sup> at the potential window of 0.054-0.150 V (vs. RHE) in 1.0 M KOH.

Sample	Overpotential @j=10 mA cm <sup>-2</sup> (mV)	Tafel slope (mV dec <sup>-1</sup> )	Reference
CoP/CC <sup>a</sup>	209	129	J. Am. Chem. Soc. <b>2014</b> , <i>136</i> (21), 7587-7590
Cu <sub>0.3</sub> Co <sub>2.7</sub> P/NC <sup>b</sup>	220	122	Adv. Energy Mater. <b>2017</b> , <b>7</b> (2), 1601555.
Co <sub>2</sub> P@NPG <sup>c</sup>	165	96	Nano Lett . <b>2016</b> , <i>16</i> (7), 4691-4698
FeP NAs/CC <sup>d</sup>	218	146	ACS Catal. <b>2014</b> , <i>4</i> (11), 4065-4069
Co-NRCNTs <sup>e</sup>	370	-	Angew. Chem. Int. Ed. <b>2014</b> , <i>53</i> (17), 4372-4376.
Co-PNCNF <sup>f</sup>	249	92	J. Mater. Chem. A. <b>2016</b> , <i>4</i> (33), 12818-12824.
WP NAs/CC <sup>g</sup>	150	102	ACS Appl. Mater. Interfaces., <b>2014</b> , <i>6</i> (24), 21874-21879.
CoP/CNF-200	141	84	This work

Table S2 Summary of various non-noble metal catalysts for HER in 1 M KOH.

<sup>a</sup> Self-supported nanoporous cobalt phosphide nanowire arrays on carbon cloth (CoP/CC);

<sup>b</sup> Bimetallic cobalt-based phosphide zeolitic imidazolate framework (BCP-ZIF);

<sup>c</sup> Dicobalt phosphide (Co<sub>2</sub>P) nanoparticles encapsulated in N, P-doped graphene;

<sup>d</sup> FeP nanorod arrays on carbon cloth (FeP NAs/CC);

<sup>e</sup> Cobalt-embedded nitrogen-rich carbon nanotubes (NRCNTs);

<sup>f</sup>Cobalt nanoparticle embedded porous nitrogen doped carbon nanofibers;

<sup>g</sup> Tungsten phosphide nanorod arrays on carbon cloth (WP NAs/CC).



**Figure S14** The theoretical models of H\* adsorbed on: (a) Graphene, (b) N-Graphene, (c) CoP, (d) CoP/Graphene and (e) CoP/N-Graphene. The grey, green, blue, violet and white balls represent C, N, Co, P and H atoms, respectively.

#### **Calculation of free energies:**

The Gibbs free energy change ( $\Delta G_{H^*}$ ) shows the following express:  $\Delta G_{H^*} = \Delta E_{H^*}$ + $\Delta E_{ZPE}$  -T $\Delta S$ , where  $\Delta E_{H^*}$ ,  $\Delta E_{ZPE}$  and  $\Delta S$  are the adsorption energy of atomic hydrogen on the given surface, zero point energy correction and entropy change of H\* adsorption, respectively. The zero point energy correction is estimated by the equation  $\Delta E_{ZPE} = E_{ZPE}(H^*) - 1/2 E_{ZPE}(H_2)$  where  $E_{ZPE}(H^*)$  and  $E_{ZPE}(H_2)$  calculated by vibration frequency calculation. At 1 bar and 298.15 K, T $\Delta S$  is approximately -0.2 eV. The value of  $\Delta E_{H^*}$  is calculated as  $\Delta E_{H^*} = E_{tot}-E_{sub}-1/2E_{H^2}$ , where  $E_{tot}$  and  $E_{sub}$  are the energies of H absorbed systems and the clean given surface, respectively, and  $E_{H^2}$  is the energy of molecular H<sub>2</sub> in the gas phase.



**Figure S15** CV curves of (a) CoP/NCF-100, (b) CoP/NCF-300, (c) CoP/NC and (d) NCF at different scan rates from 5 to 25 mV·s<sup>-1</sup> at the potential window of 1.4-1.5 V (vs. RHE) in 1.0 M KOH.



**Figure S16** High resolution (a) Co 2p and (b) P 2p XPS spectra of the CoP/NCF-200 before and after 10 h stability test for OER.



Figure S17 The XRD spectra of CoP/NCF-200 after 10 h stability test for OER.

Sample	Overpotential	Tafel slope	Reference
	@j=10 mA cm <sup>-2</sup> (mV)	$(mV \cdot dec^{-1})$	
Co/CoP-5 <sup>a</sup>	340	79.5	Adv. Energy Mater. <b>2017</b> , 7 (12), 1602355.
CoP film <sup>b</sup>	345	47	Angew. Chem. Int. Ed. <b>2015</b> , <i>54</i> (21), 6251-6254.
CoMnP <sup>c</sup>	330	61	J. Am. Chem. Soc. <b>2016</b> , <i>138</i> (12), 4006-4009.
Co/CoP-HNC <sup>d</sup>	300	53.6	Mater. Horiz. <b>2018</b> , <i>5</i> (1), 108-115.
CP/CTs/Co-S <sup>e</sup>	306	72	ACS Nano. <b>2016</b> , <i>10</i> (2), 2342-2348.
Co-P@NC-800 <sup>f</sup>	370	79	ACS Appl. Mater. Interfaces. <b>2017</b> , <i>9</i> (46), 40171-40179.
Co <sub>2</sub> P/Co-foil <sup>g</sup>	319	79	J. Mater. Chem. A. <b>2017</b> , <i>5</i> (21), 10561-10566.
CoP/CNF-200	288	60	This work

Table S3 Summary of various non-noble metal catalysts for OER in 1.0 M KOH.

<sup>a</sup> Carbon coated metallic Co nanoparticles into Co/CoP Janus nanoparticles;

<sup>b</sup>Cobalt-phosphorous-derived (Co-P) films on copper foil;

<sup>c</sup> Ternary cobalt manganese phosphide nanoparticles;

<sup>d</sup> Co/CoP embedded in a hairy nitrogen-doped carbon polyhedral (Co/CoP–HN C);

<sup>e</sup> An integrated three-dimensional (3D) electrode of carbon paper/carbon

tubes/cobalt-sulfide sheets (denoted as CP/CTs/Co-S);

<sup>f</sup> Cobalt phosphide nanoparticles embedded in N-doped carbon materials (Co-P@NC);

<sup>g</sup> Cobalt-rich cobalt phosphide catalysts directly grown on cobalt foil;

	Voltages		
Sample	@j=10 mA cm <sup>-2</sup> (V)	Reference	
Ni <sub>3</sub> S <sub>2</sub> /NF <sup>a</sup>	1.76	J. Am. Chem. Soc. <b>2015</b> , <i>137</i> (44), 14023-14026.	
CP/CTs/Co-S <sup>b</sup>	1.743	ACS Nano. <b>2016</b> , <i>10</i> (2), 2342-2348.	
CoP/rGO-400 °	1.68	Chem. Sci. <b>2016</b> , 7 (3), 1690-1695.	
EG/Co <sub>0.85</sub> Se/NiFe-LDH <sup>d</sup>	1.67	Energy Environ. Sci. <b>2016</b> , <i>9</i> (2), 478-483.	
Ni-P/CF <sup>e</sup>	1.68	J. Power Sources. <b>2015</b> , <i>299</i> , 342-346.	
Fe <sub>0.4</sub> Co <sub>0.6</sub> <sup>f</sup>	1.68	Nano Energy. <b>2017</b> , <i>38</i> , 576-584.	
CoP/PNC <sup>g</sup>	1.68	Carbon .2019, 144, 464-471.	
CoP/CNF-200/NF	1.64	This work	

Table S4 Summary of various catalyts for overall water splitting in 1.0 M KOH.

<sup>a</sup> In situ growth of  $\{210\}$  high-index faceted Ni<sub>3</sub>S<sub>2</sub> nanosheet arrays on nickel foam (NF);

<sup>b</sup>An integrated three-dimensional (3D) electrode of carbon paper/carbon tubes/cobalt-sulfide sheets (denoted as CP/CTs/Co-S);

<sup>c</sup> A layered CoP/reduced graphene oxide (rGO) composite;

- <sup>d</sup> In situ growth of cobalt selenide ( $Co_{0.85}Se$ ) nanosheets vertically oriented on electrochemically exfoliated graphene foil, with subsequent deposition of NiFe layered- double-hydroxide by a hydrothermal treatment;
- <sup>e</sup> Nickel-phosphorus nanoparticles film on copper foam (Ni-P/CF);
- <sup>f</sup>Fe-Co composite films on carbon fiber papers (CFPs);
- <sup>g</sup> N-doped carbon shell coated CoP nanocrystals encapsulated in porous carbon substrate.

#### **Reference:**

Gao, W.; Yan, M.; Cheung, H.Y.; Xia, Z.; Zhou, X.; Qin, Y.; Wong, C.Y.; Ho, J.
 C.; Chang, C.R.; Qu, Y. Modulating electronic structure of CoP electrocatalysts towards enhanced hydrogen evolution by Ce chemical doping in both acidic and basic media. *Nano Energy* 2017, *38*, 290-296, DOI 10.1016/j.nanoen.2017.06.002.

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