

## **Electronic Supplementary Information**

# **Needle Grass-like Cobalt Hydrogen Phosphate on Ni Foam as Effective and Stable Electrocatalysts for Oxygen Evolution Reaction**

Zemin Sun,<sup>#</sup> Mengwei Yuan,<sup>#</sup> Liu Lin, Han Yang, Huifeng Li, Genban Sun,<sup>\*</sup> Xiaojing Yang, Shulan Ma

Beijing Key Laboratory of Energy Conversion and Storage Materials, College of Chemistry, Beijing Normal University, Beijing 100875, China

### **Corresponding Author**

\*E-mail: gbsun@bnu.edu.cn

## **Experimental section**

### **Preparation of CoHPO/NF electrode**

4 mmol  $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ , 4 mmol  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  and 2 mmol  $\text{CON}_2\text{H}_4$  were added and dissolved in 80 mL deionized  $\text{H}_2\text{O}$ . After 10 minutes ultrasound, the solution and the Ni foam were transferred to a Teflon-lined autoclave and then it was heated at 120 °C for 12 h. The powder in the Teflon-lined autoclave was collected and washed *via* water and ethanol. The CoHPO/NF electrode was ultrasonicated with water and ethanol several times. Both powder and CoHPO/NF electrode were dried at 80 °C overnight.

### **Preparation of Co(OH)<sub>2</sub>/NF electrode**

The preparation of  $\text{Co(OH)}_2/\text{NF}$  was similar to that of CoHPO/NF, except for the addition of  $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ .

### **Preparation of RuO<sub>2</sub> -NF electrode**

$\text{RuO}_2$  (4 mg) was dispersed in a 1 mL mixed solution, including 490  $\mu\text{L}$   $\text{H}_2\text{O}$ , 15  $\mu\text{L}$  Nafion solution (5 wt %), and 495  $\mu\text{L}$  EtOH, and then followed by sonication to form a uniform catalyst ink. Put the as-prepared ink (100  $\mu\text{L}$ ) on the Nickel Foam (area: 1 cm $\times$ 1 cm). Finally, the electrode was dried at 80 °C overnight.

### **Preparation of CoHPO -NF electrode**

CoHPO (4 mg) was dispersed in a 1 mL mixed solution, including 490  $\mu\text{L}$   $\text{H}_2\text{O}$ , 15  $\mu\text{L}$  Nafion solution (5 wt %), and 495  $\mu\text{L}$  EtOH, and then followed by sonication to form a uniform catalyst ink. Put the as-prepared ink (100  $\mu\text{L}$ ) on the Nickel Foam (area: 1 cm $\times$ 1 cm). Finally, the electrode was dried at 80 °C overnight.

### **Preparation of CoHPO /CP electrode**

The preparation of CoHPO/CP was similar to that of CoHPO/NF, except for replacing nickel foam with carbon Paper (CP).

### **Materials characterization**

The morphologies were tested through Hitachi field emission scanning electronic microscope. Micromorphology and fine structure were measured *via* FEI Tecnai F20 field emission transmission electron microscope. The crystal structure was confirmed by Phillips X'pert ProMPD diffractometer. Nicolet-380 Fourier transform infrared spectrometer was used to test Fourier transform infrared spectroscopy (FT-IR). An ESCALAB 250Xi spectrometer (Thermo Fisher) was employed to measure the X-Ray photoelectron spectra (XPS). The loading of CoHPO was measured using inductively coupled plasma mass spectroscopy (Thermo XSeries II) by dissolving 1 cm × 1 cm electrode in 100 mL aquaregia.

### **Electrochemical measurements**

Zennium IM6 station was applied to conduct electrochemical measurements in 1.0 M KOH. The linear sweep voltammetry (LSV) curves were scanned at 5 mV s<sup>-1</sup> in a standard three-electrode system. The Pt wire and Hg/HgO electrode acted as the counter electrode and the reference electrode, and as-prepared Ni Foam was the working electrode. The conversion of the potential value to reversible hydrogen electrode (RHE) was based on the formula:  $\eta = E_{\text{RHE}} - 1.23 \text{ V}$ . Electrochemical impedance spectroscopy (EIS) was measured in the frequency range from 10 mHz to 100 kHz.

### **Calculation Methods**

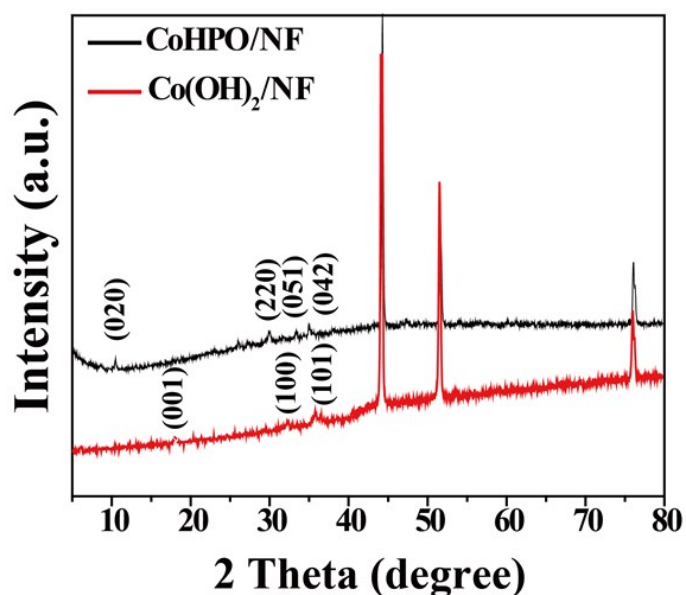
Based on the spin polarized density functional theory (DFT) and the projector augmented wave (PAW) method as implemented in the Vienna Ab-initio Simulation Package (VASP), the density of

states were calculated by the strongly constrained and appropriately normed (SCAN) functional within the meta-generalized-gradient approximation (meta-GGA). A plane-wave basis set was used with kinetic energy cutoff of 400 eV with a K-point grid of  $2 \times 2 \times 4$  and  $4 \times 4 \times 4$  for CoHPO and  $\text{Co}(\text{OH})_2$ , respectively, using the Gamma centered method. A plane-wave basis set with an energy cutoff of 400 eV was used with a  $0.01 \text{ eV/\AA}$  convergence threshold on each atom for force. All the adsorption models for CHPO and  $\text{Co}(\text{OH})_2$  were created and cut along the (001) direction. To avoid the interaction between two neighboring images, the vacuum space along the z axis was set to be 10  $\text{\AA}$ .

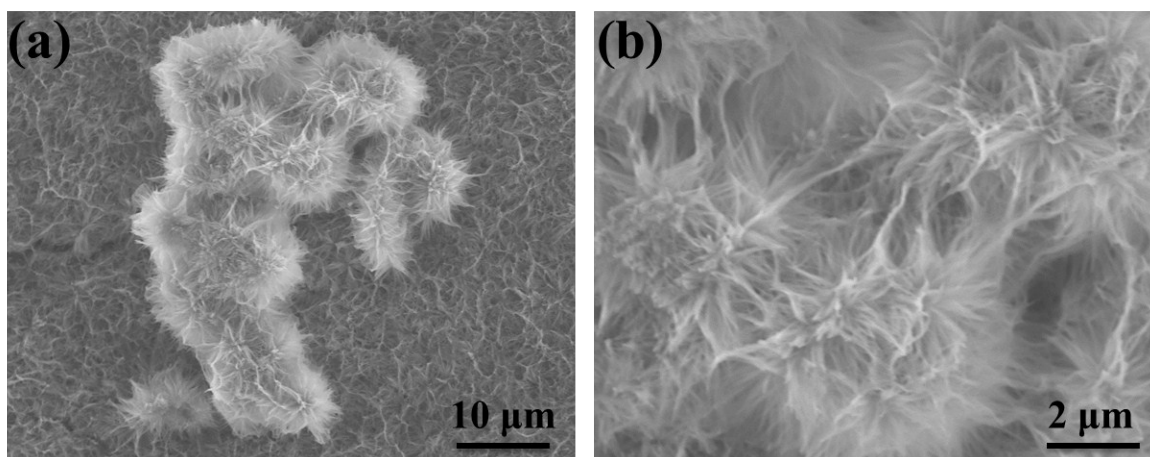
The adsorption energies of OH groups on two substrates were defined as:

$$E_{\text{ads}} = E_{\text{system}} - E_{\text{substrate}} - E_{\text{OH}}$$

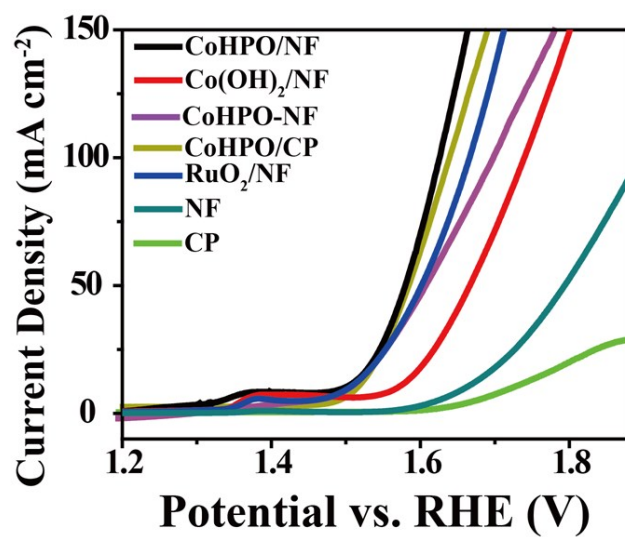
where  $E_{\text{system}}$  is the DFT calculated energy of the adsorption system, the  $E_{\text{substrate}}$  is the energy of the substrate, and  $E_{\text{OH}}$  means the energy of OH.



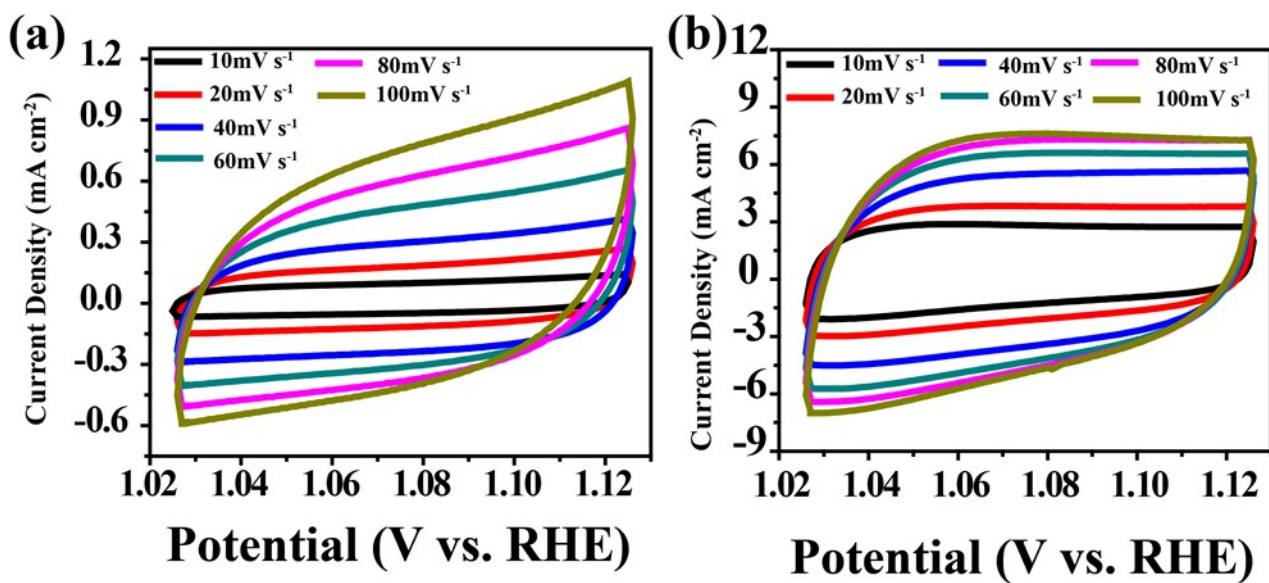
**Figure S1.** XRD of CoHPO/NF and  $\text{Co}(\text{OH})_2/\text{NF}$



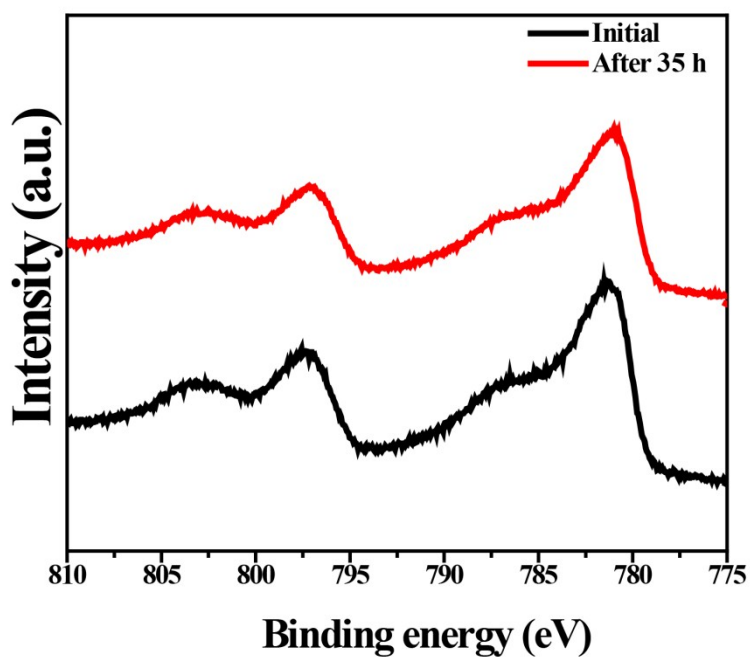
**Figure S2.** SEM of  $\text{Co(OH)}_2$  at low (a) and high (b) magnification



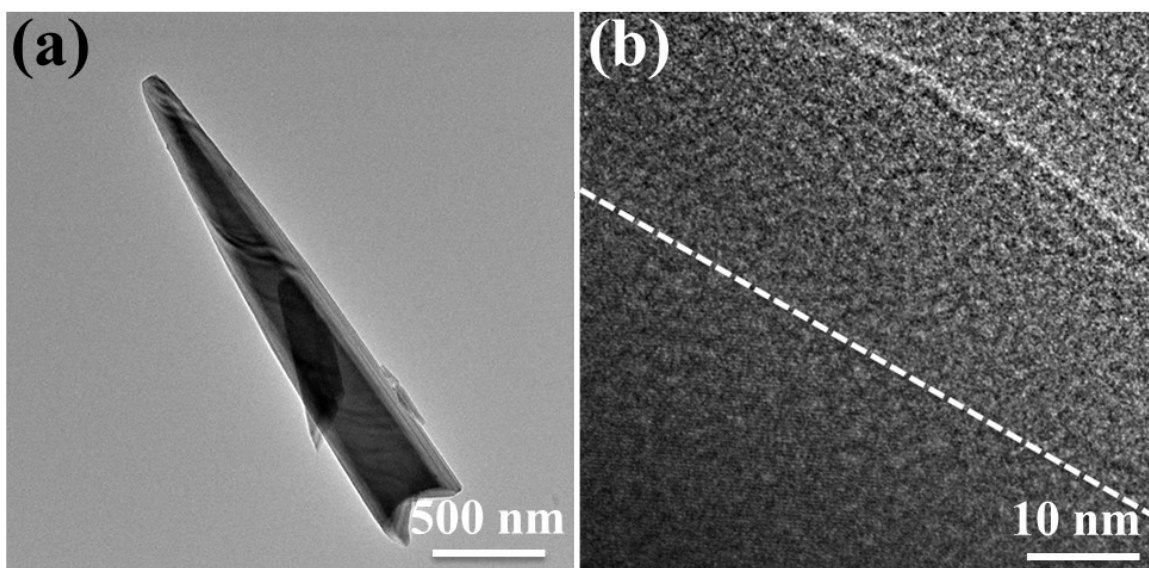
**Figure S3** Polarization curves of CoHPO/NF,  $\text{Co(OH)}_2/\text{NF}$ , CoHPO-NF, CoHPO/CP,  $\text{RuO}_2/\text{NF}$ , NF and Carbon paper.



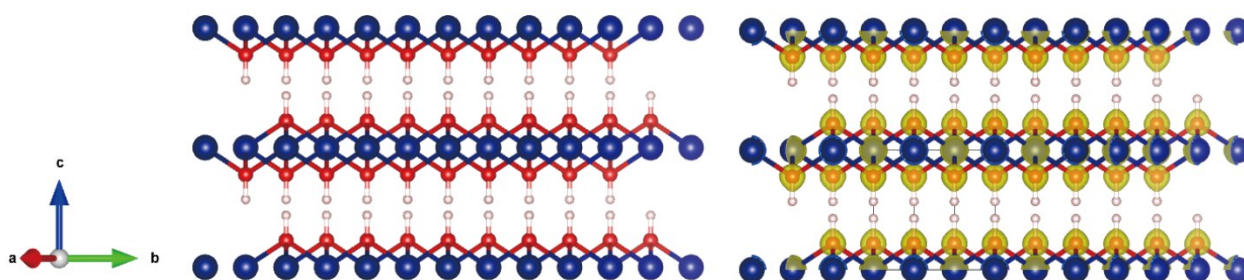
**Figure S4** CVs of Co(OH)<sub>2</sub>/NF (a) and CoHPO/NF (b) in the non-faradaic capacitance current range at scan rates of 10, 20, 40, 60, 80, and 100 mV s<sup>-1</sup>.



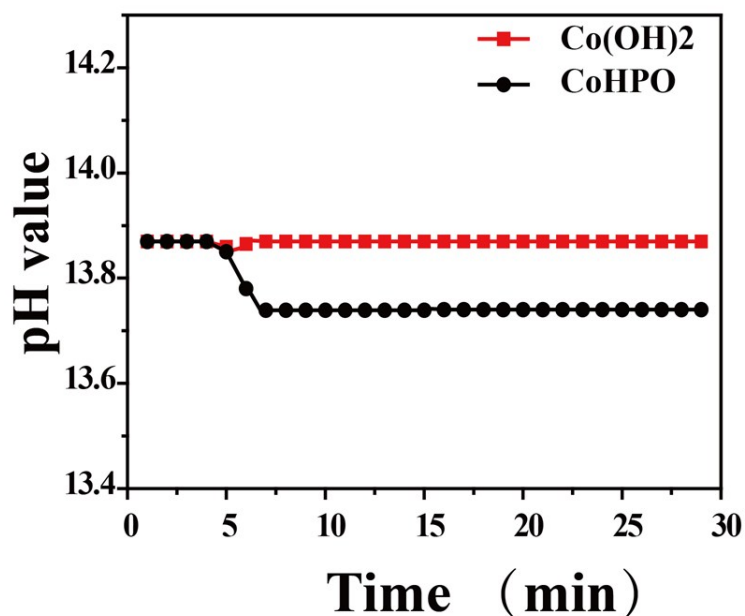
**Figure S5** XPS Co spectra of the CoHPO/NF for initial electrode and after OER durability tests.



**Figure S6** TEM (a) and HRTEM (b) for CoHPO after OER durability tests.



**Figure S7** The crystal structure of the Co(OH)<sub>2</sub> and corresponding structure with ELF isosurfaces



**Figure S8** The pH value-time curve with CoHPO and Co(OH)<sub>2</sub> added in the fifth min (the same weight CoHPO and Co(OH)<sub>2</sub> powder in the same volume of solution (0.1 mg/ml).

**Table S1** the ICP for initial CoHPO/NF and Co(OH)<sub>2</sub>/NF after OER test

Sample	CoHPO/NF	Co(OH) <sub>2</sub> /NF
Co (μg ml <sup>-1</sup> )	1.21	2.44

**Table S2** Comparison of the electrocatalytic OER activity of CoHPO/NF to other oxide/hydroxide-based OER catalysts in 1 M KOH

Catalyst	j(mAcm <sup>-2</sup> )	η (mV)	Electrolyte	Ref.
CoHPO/NF	50	350	1M KOH	This work
CoHPO/NF	100	395	1M KOH	This work
CoFe-LDH	50	360	1M KOH	Chem. Sci., 2015, 6, 6624.
Co@Co <sub>3</sub> O <sub>4</sub> -NC	10	391	1M KOH	J. Mater. Chem. A, 2017, 5, 9533-9536
CoSe <sub>2</sub> -NC	50	450	1M KOH	ACS Appl. Mater. Interfaces 2019, 11, 3372



NiCo LDHs	50	370	1M KOH	Nano Lett. 2015, 15, 1421
Co <sub>5</sub> Mn-LDH/MWCNT	50	410	1M KOH	ACS Appl. Mater. Interfaces 2016, 8, 14527
Cu <sub>0.3</sub> Co <sub>2.7</sub> P/NC	50	~350	1M KOH	Adv. Energy Mater. 2017, 7, 1601555
Cu@NCNT/Co <sub>x</sub> O <sub>y</sub>	10	370	1M KOH	Adv. Funct. Mater. 2017, 27, 1605717
NiCo LDHs	50	430	1 M KOH	Nano Lett. 2015, 15,1421

**Table S3** the ICP for initial and after durability tests CoHPO/NF.

Sample	Innial	after durability tests
Co ( $\mu\text{g ml}^{-1}$ )	1.21	1.21