

## Supporting Information

# Heterogeneous Co(OH)<sub>2</sub> Nanoplates/Co<sub>3</sub>O<sub>4</sub> Nanocubes Enriched with Oxygen Vacancies Enable Efficient Oxygen Evolution Reaction Electrocatalysis

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## Experimental section

### Chemical and reagents

Cobalt nitrate (Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, analytical reagent), ethanol (CH<sub>3</sub>CH<sub>2</sub>OH, 99%), PVP (Mw. 55000), hexamethylenetetramine (HMT), KOH, Nafion, and isopropanol were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All chemicals were used as purchased without further purification.

### Synthesis of Co(OH)<sub>2</sub> nanoplates

In a typical synthesis, 0.582 g Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 0.2 g PVP (Mw. 55000), and 0.28 g hexamethylenetetramine (HMT) were dissolved in 80 mL of a 9:1 mixture of deionized H<sub>2</sub>O and ethanol. The reaction solution was then refluxed at about 95 °C for 2 h. The nanoplates were then isolated by centrifugation and washed with water several times.

### Synthesis of Co<sub>3</sub>O<sub>4</sub> nanocubes

0.291 g Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was dissolved in 20 mL 0.1 M NaOH solution. The obtained

solution was transferred into 100 mL autoclave with a Teflon liner at 200 °C, and kept for 24 h. The obtained product was filtered, and then washed with H<sub>2</sub>O and ethanol for several times, and dried naturally in air.

#### **Typical preparation of Co(OH)<sub>2</sub> nanoplates/Co<sub>3</sub>O<sub>4</sub> nanocubes**

0.150 g Co(OH)<sub>2</sub> nanoplates and 0.080 g Co<sub>3</sub>O<sub>4</sub> nanocubes were dispersed into 10 mL ethanol, and then was sonicated for 60 min to form a black mixture. The obtained mixture was filtered, and dried in air naturally.

#### **Characterizations**

Transmission electron microscope (TEM) was conducted on a HITACHI HT7700 at an acceleration voltage of 120 kV. Energy dispersive X-ray (EDX) patterns were carried out on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. Powder X-ray diffraction (PXRD) patterns were collected on X'Pert-Pro MPD diffractometer (Netherlands PANalytical) with a Cu K $\alpha$  X-ray source ( $\lambda = 1.540598 \text{ \AA}$ ). X-ray photoelectron spectroscopy spectra (XPS) were conducted on a Thermo Scientific ESCALAB 250 XI X-ray photoelectron spectrometer. The inductively coupled plasma atomic emission spectroscopy (ICP-AES) was also conducted to study the compositions of the samples.

#### **Electrochemical measurements**

The electrochemical properties of the samples were measured with a CHI 660e electrochemistry workstation using a standard three-electrode cell at room temperature. The sample-coated glassy carbon electrode, a Ag/AgCl electrode, and a carbon rod were selected as working electrode, a reference electrode, and a counter electrode, respectively. To prepare the working electrode, 2 mg samples were first dissolved in a solution (1:9, v/v) containing Nafion (5%) and water (2 mL) by sonication. Then, 20  $\mu$ L freshly prepared suspension was dropped on the surface of pre-polished glassy carbon electrode (GCE, 3 mm in diameter) and dried at room temperature for 12 h before measurements. For comparison, the Ir/C catalysts (20 wt%, 2-5 nm Ir nanoparticles) purchased from Johnson Matthey (JM) Corporation were selected as the reference catalyst. Before the OER tests, the cyclic voltammetry

(CV) for these electrocatalysts were operated in 1.0 M KOH solution at the scanning rate of 50 mV s<sup>-1</sup> to activate the electrocatalysts. The polarization curves were acquired using linear sweep voltammetry (LSV) for OER in 1.0 M KOH solution at the scanning rate of 5 mV s<sup>-1</sup>. iR drop was compensated at 95% for measurements. The Tafel plots were derived from the OER polarization curves (1 mV s<sup>-1</sup>) and constructed by the Tafel equation. It is worth noting that all the potentials measured were calibrated to reverse hydrogen electrode (RHE) and the state-of-the-art Ir/C catalyst was also employed as the baseline catalysts for all the electrochemical measurements.

### **Calculation of ECSA**

The calculation of the electrochemical surface areas (ECSA) are based on the measured double layer capacitance of the catalysts modified electrode in 1.0 M KOH according to previous published report. Briefly, a potential range where no apparent Faradaic process happened was determined firstly using the static CV. The charging current  $i_c$  was measured from the CVs at different scan rates. The relation between  $i_c$ , the scan rate ( $v$ ) and the double layer capacitance ( $C_{DL}$ ) was given in eq 1. Therefore, the  $C_{DL}$  is then calculated according to:  $C_{DL} = d(\Delta j(0 \text{ V vs. RHE}))/2dv$ .

$$i_c = v C_{DL} \quad (1)$$

For the estimation of ECSA, a specific capacitance ( $C_S$ ) value  $C_S = 0.040 \text{ mF cm}^{-2}$  in 1.0 M KOH.

$$\text{ECSA} = C_{DL} / C_S \quad (2)$$

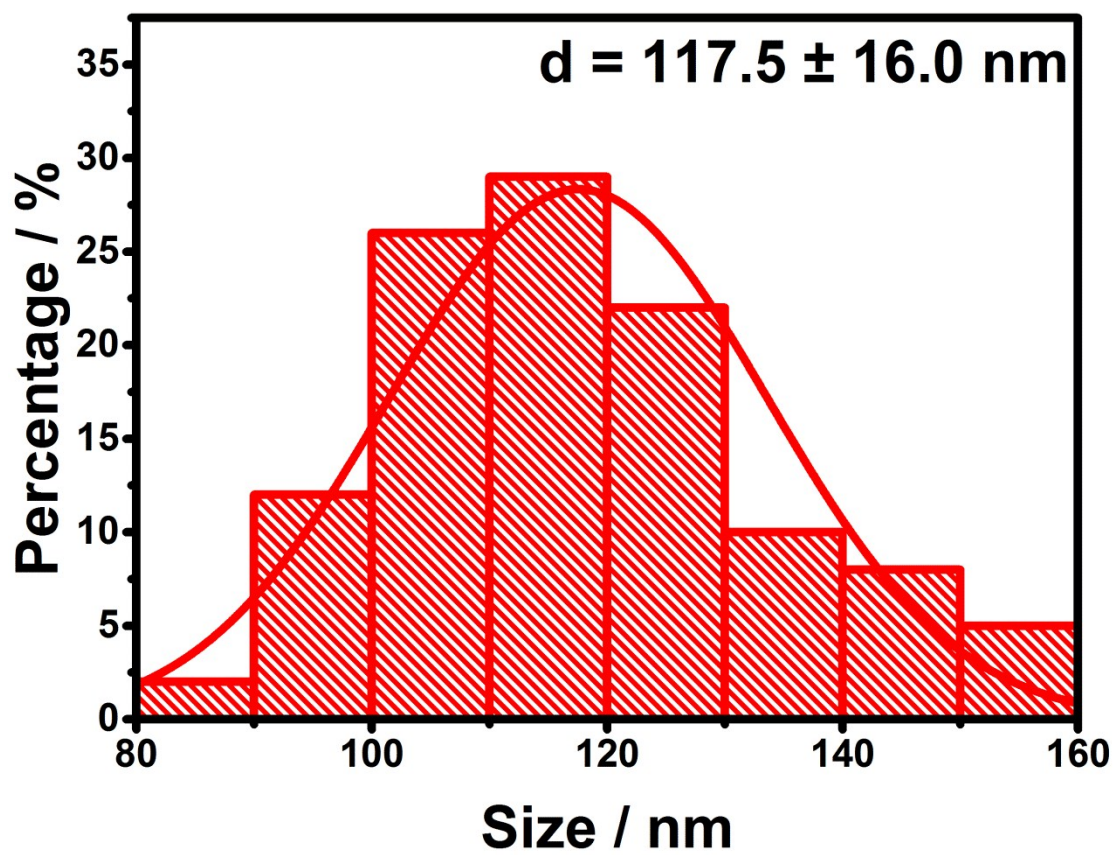


Fig.S1 Size distribution of Co(OH)<sub>2</sub> NPs.

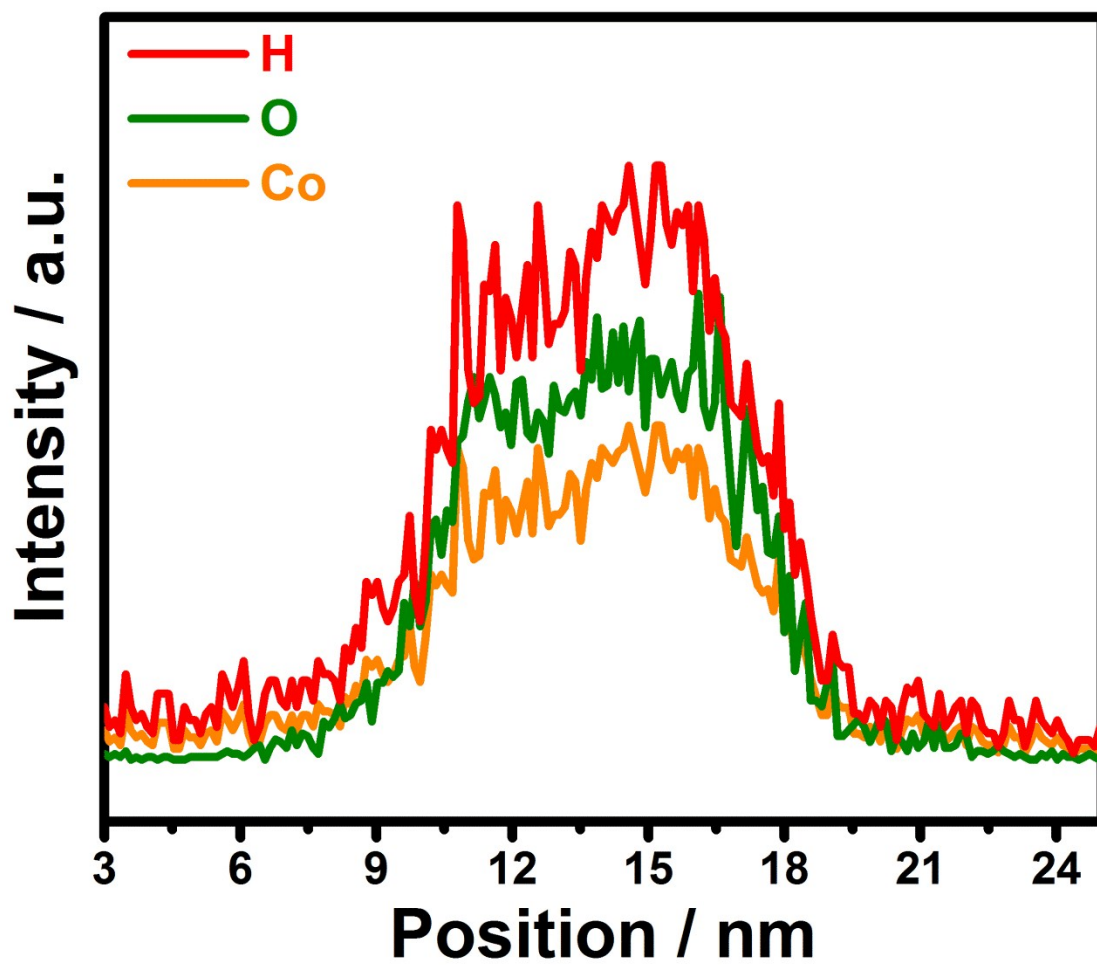


Fig.S2 Elemental line-scan profile of Co(OH)<sub>2</sub> NPs.

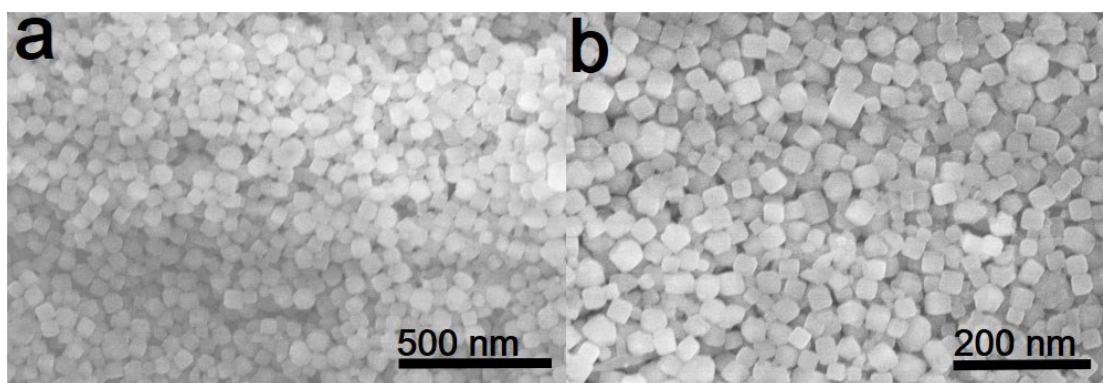


Fig.S3 Representative SEM images of Co<sub>3</sub>O<sub>4</sub> NCs with different magnifications.

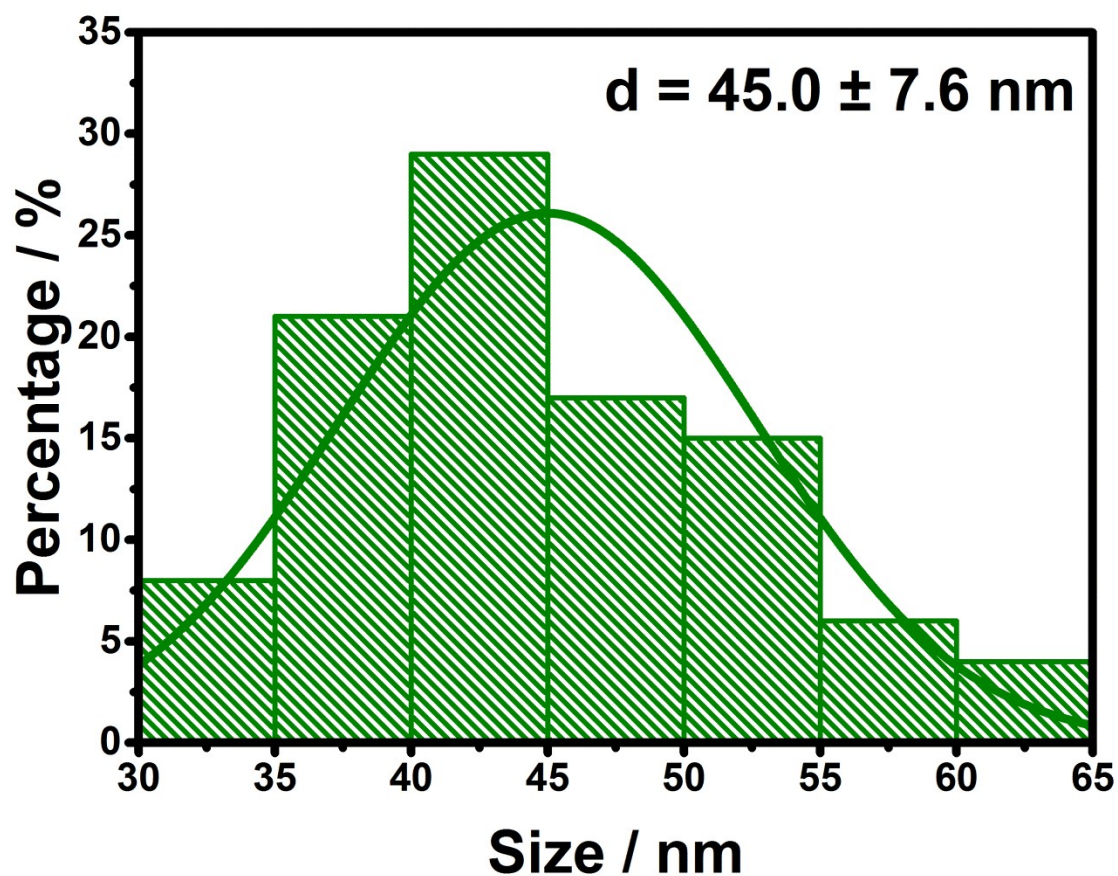


Fig.S4 Size distribution of  $\text{Co}_3\text{O}_4$  NCs.

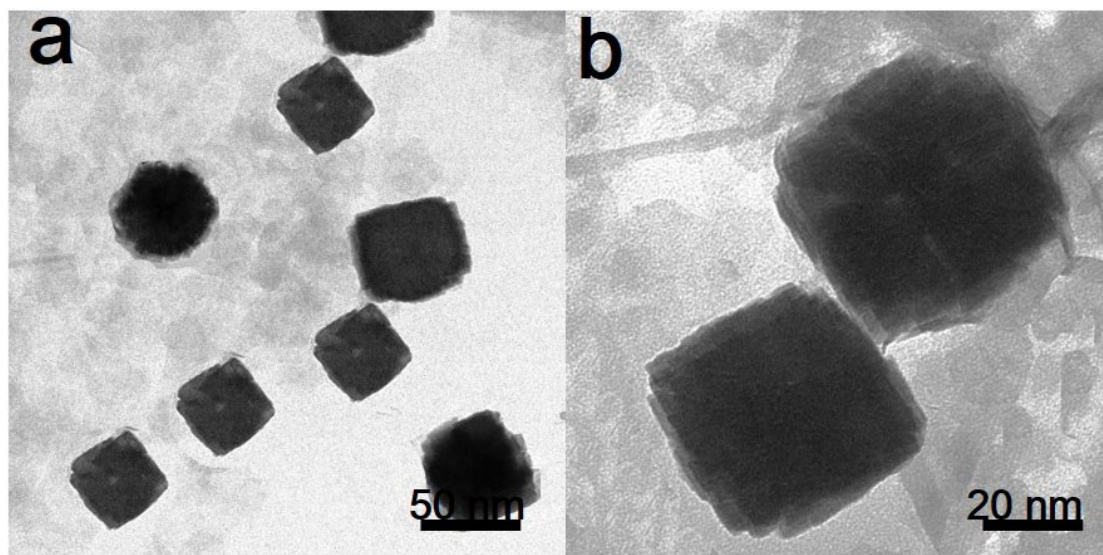


Fig.S5 Representative TEM images of  $\text{Co}_3\text{O}_4$  NCs with different magnifications.



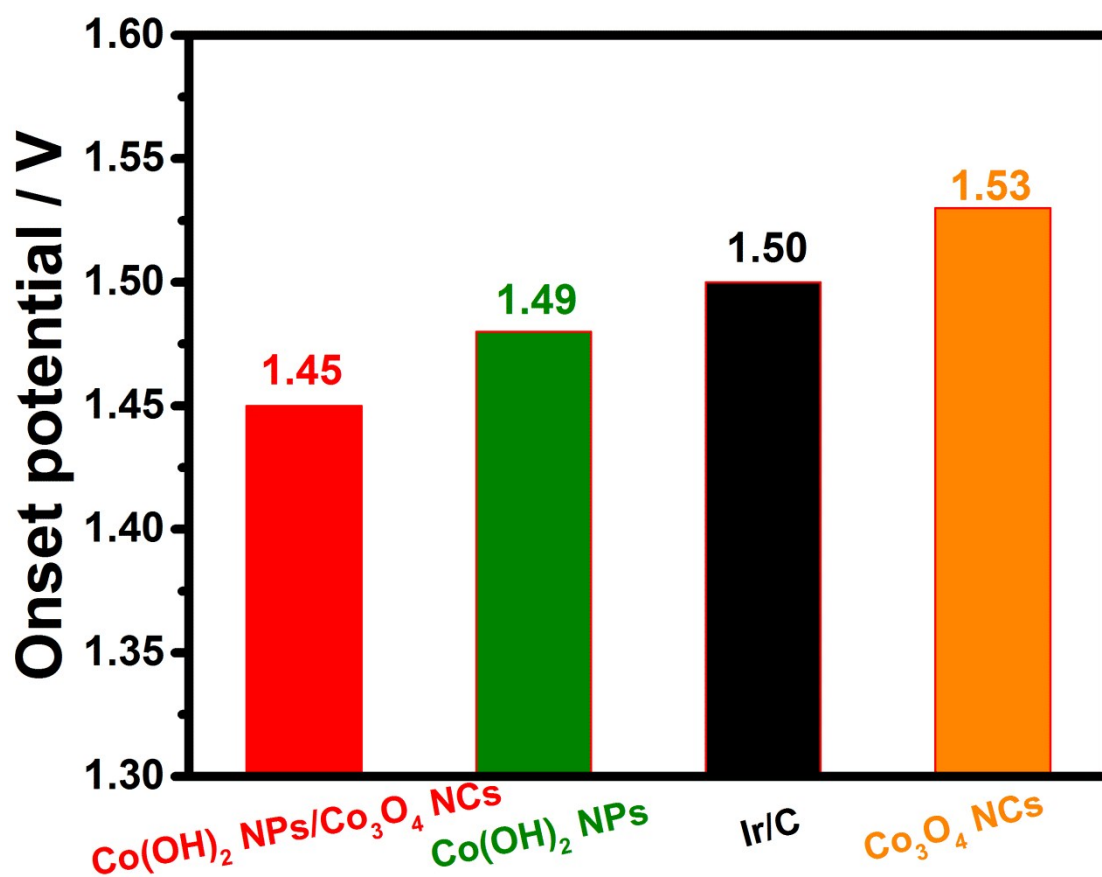


Fig.S6 Onset potentials of  $\text{Co(OH)}_2$  NPs/ $\text{Co}_3\text{O}_4$  NCs,  $\text{Co(OH)}_2$  NPs, Ir/C, and  $\text{Co}_3\text{O}_4$  NCs.

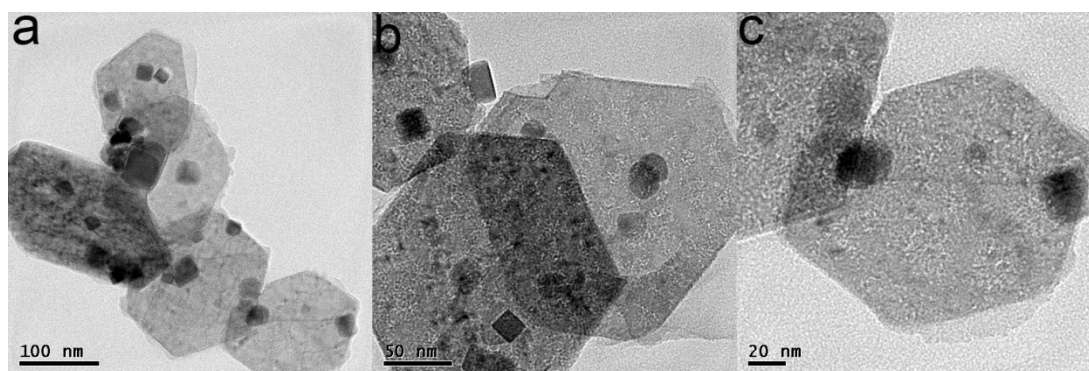


Fig.S7 Representative TEM images of  $\text{Co(OH)}_2$  NPs/ $\text{Co}_3\text{O}_4$  NCs with different magnifications after long-term electrochemical test.

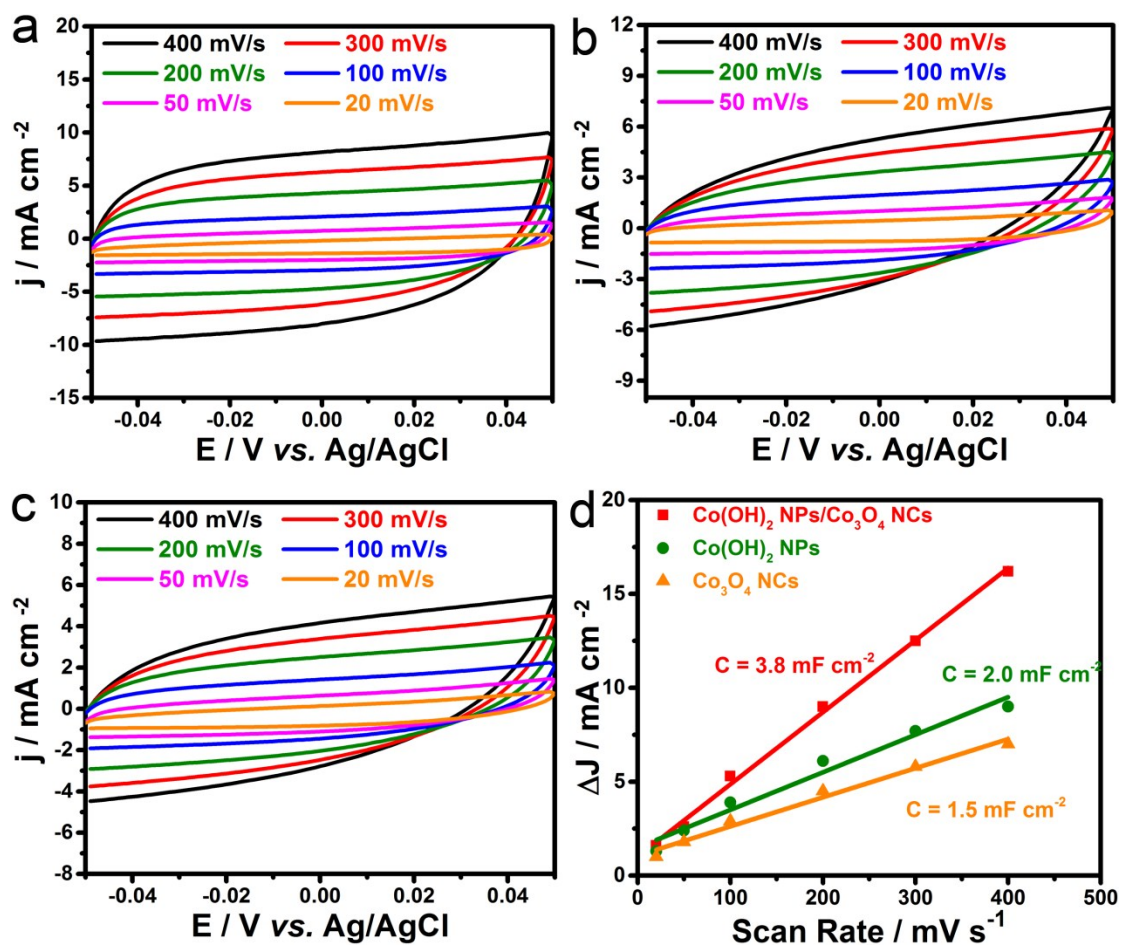


Fig.S8 CV curves of (a) Co(OH)<sub>2</sub> NPs/Co<sub>3</sub>O<sub>4</sub> NCs, (b) Co(OH)<sub>2</sub> NPs, and (c) Co<sub>3</sub>O<sub>4</sub> NCs with different scan rates and (d) their double layer currents vs scan rates plots.



**Table S1** Comparisons of OER activity for various electrocatalysts in alkaline condition ( $\eta$ : overpotential at the current density of 10 mA cm<sup>-2</sup>).

Catalyst	$\eta$ (mV)	Electrolyte	Reference
<b>Co(OH)<sub>2</sub> NPs/Co<sub>3</sub>O<sub>4</sub> NCs</b>	<b>281</b>	1.0 M KOH	<b>This work</b>
<b>Co<sub>3</sub>O<sub>4</sub>/Co(OH)<sub>2</sub> hybrids</b>	370	1.0 M KOH	New J. Chem. 2018, 42, 4215
<b>CoFeP NSs</b>	305	1.0 M KOH	J. Colloid Interface Sci.2 2018, 530, 146
<b>CoO<sub>x</sub>-ZIF</b>	318	1.0 M KOH	Adv. Funct. Mater. 2017, 1702546
<b>IrO<sub>x</sub></b>	370	1.0 M KOH	J. Am. Chem. Soc.2012, 134, 17253
<b>NF@NC-CoFe<sub>2</sub>O<sub>4</sub></b>	350	1.0 M KOH	Adv. Mater. 2017, 29, 1604437
<b>Co@Co-Bi/Ti</b>	327	1.0 M KOH	Nanoscale 2017, 9, 16059
<b>Co<sub>3</sub>O<sub>4</sub>@CoO SC</b>	430	1.0 M KOH	Nat. Commun. 2015, 6, 8
<b>Ni<sub>3</sub>Se<sub>4</sub></b>	320	1.0 M KOH	Nanoscale 2018, 10, 5163
<b>ZnCo LDH</b>	>330	1.0 M KOH	J. Mater. Chem. A, 2014, 2, 13250
<b>NiZnP NSs</b>	290	1.0 M KOH	J. Colloid Interface Sci.2 2018, 530, 58
<b>Fe<sub>3</sub>O<sub>4</sub> cubes</b>	336	1.0 M KOH	ACS Energy Lett. 2018, 3, 861-868
<b>Ir<sub>0.46</sub>Co<sub>0.54</sub>O<sub>y</sub> nanotubes</b>	310	1.0 M NaOH	ACS Appl. Mater. Interface, 2017, 9, 35057
<b>Ni<sub>5</sub>P<sub>4</sub></b>	470	1.0 M KOH	Angew. Chem. Int. Ed. 2015, 54, 12361
<b>CoMn LDH</b>	324	1.0 M KOH	J. Am. Chem. Soc. 2014, 136, 16481
<b>NiCo-LDH</b>	290	1.0 M KOH	J. Power Sources 2015, 278, 445-451
<b>CoO<sub>x</sub>-ZIF</b>	318	1.0 M KOH	Adv. Funct. Mater. 2017, 1702546
<b>Titanium carbide-CoBDC</b>	410	0.1 M KOH	ACS Nano, 2017, 11, 5800
<b>MAF-X27-OH</b>	387	1.0 M KOH	J. Am. Chem. Soc.2016, 138, 8336
<b>CoSe<sub>2</sub> nanosheets</b>	320	0.1 M KOH	J. Am. Chem. Soc. 2014, 136, 15670
<b>Ni-Co oxides layers</b>	325	1.0 M KOH	ACS Nano 2014, 8, 9518
<b>RuO<sub>2</sub></b>	387	0.1 M KOH	J. Am. Chem. Soc. 2014, 136, 7077

<b>Au@Co<sub>3</sub>O<sub>4</sub></b>	378	1.0 M KOH	Adv. Mater. 2014, 26, 3950
<b>Co<sub>3</sub>O<sub>4</sub>@CoO SC</b>	430	1.0 M KOH	Nat. Commun. 2015, 6, 8.
<b>Ni-Co oxides layers</b>	325	1.0 M KOH	ACS Nano 2014, 8, 9518