Supporting Information

Nickel/Cobalt Oxide as High Efficient OER Electrocatalyst in Alkaline Polymer Electrolyte Water Electrolyser

Jun Chi [a,b], Hongmei Yu [a,*], Guangfu Li,[a,b] Li Fu [a,b], Jia Jia [a,b], Xueqiang Gao [a,b], Baolian Yi [a], Zhigang Shao [a,*]

Laboratory of Fuel Cells, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Zhongshan Road 457, Dalian 116023, China.

*E-mail: hmyu@dicp.ac.cn; zhgshao@dicp.ac.cn;

Tel.: +86-411-84379051;

Fax: +86-411-84379185

S1. Experimental Section.

Synthesis of nickel oxide/cobalt oxide (NiO/CoO) hexagon nanoplate

The nickel hydroxide/cobalt hydroxide nano-hybrid is synthesized via a hydrothermal process. 0.7 mmol (0.203 g) of $Ni(NO_3)_2 \cdot 6H_2O$ ($\geq$98.0 wt.%, Da Mao Chemical Reagent Company) and 0.3 mmol (0.087 g) of $Co(NO_3)_2 \cdot 6H_2O$ ($\geq$99.0 wt.%, Xi Long Chemical Reagent Company) were added into 20 mL of distilled water in a beaker under magnetic stirring. After 10 minutes of stirring, 10 mL of ethanol ($\geq$99.7 wt.%, Shen Yang Chemical Reagent Company) and 2 mL oleylamine ($\geq$97.5 wt.%, J&K) were slowly added, and the stirring was continued for about 30 minutes to produce a homogeneous liquid. The prepared solution was then transferred into a 50 mL Teflon-lined autoclave. The autoclave was sealed and maintained at 100~200 ^oC for 5~15 h in a convection oven and then cooled to room temperature. The resulting sample was collected, centrifuged and washed with ethanol and distilled water to remove organics, ions, then dried under vacuum at 60 ^oC for 10 h. The as-synthetic samples were subsequently calcined in air at 400 ^oC for 2 h to further remove the residual surfactant and promote Ni/Co oxide alloy formation. The powder products were remarked as $Ni_nCo_{1-n}O_x$, where n (1, 0.7, 0.5, 0.3, and 0) is the mole ratio of the Ni in the solution.

Characterization of the catalysts

The phase analysis of the sample was measured by X-ray diffraction (XRD, PANalytical X'Pert PRO) via Cu-Kα tube, operated at 40 kV, and 40 mA. The scanning rate was 10° min^{-1} from 10° to 90° in 2θ. Scanning electron microscopy (SEM) images and energy-dispersive X-ray analysis (EDX) were obtained using a JSM-7800F field emission scanning electron microscope (FE-SEM) equipped with an EDX system. The morphologies of the samples were further analyzed by transmission electron microscopy (TEM). TEM images were obtained on a JEM-2000EX electron microscope, operated at an acceleration voltage of 120 kV.

Mercuric oxide electrode (MMO) was used as the reference electrode in all measurements. It was calibrated with respect to reversible hydrogen electrode (RHE)[1]. The potentials reported in our work were referenced to the RHE, and in 1 M KOH, E (V vs. RHE) = E (V vs. MMO) + 0.904 V.

The fabrication of working electrode was as follows: 5 mg of sample was dispersed in 1 mL ethanol, followed by the addition of 20 μL 5% Nafion solution. The mixture was then ultra-sonicated for about 0.5 h to obtain a homogeneous ink. 5 μL the resulting ink was carefully dropped onto the RDE, leading to a catalyst loading of ~0.2 mg cm^{-2}. The as prepared catalyst film was dried at room temperature.

Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were performed at room temperature with a CHI730 Instrument Potentialstat (Shanghai Chen Hua Instrument Co.,

Ltd.). The CV and LSV curves were obtained by sweeping the potential from 0.904 to 1.904 V vs RHE at room temperature with a scan rate of 10 mV s^{-1} and 1600 rpm.

S2 Electrochemical Measurements:

All of the electrochemical tests were carried out in a three-electrode system on an electrochemical workstation (Gamry Interface 5000E). Mercuric oxide electrode (MMO) was used as the reference electrode in all measurements. It was calibrated with respect to reversible hydrogen electrode (RHE)[1].

We used mercuric oxide electrode (MMO) (1 M KOH) as the reference electrode in all measurements. The calibration was performed in the hydrogen saturated 1 M KOH with a Pt foil as the working electrode. CVs were run at a scan rate of 1 mV s^{-1}. The potentials reported in our work were referenced to the RHE, and in 1 M KOH,
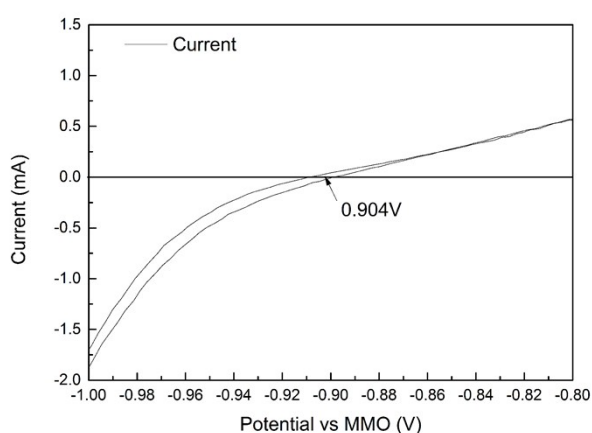
E (V vs. RHE) = E (V vs. MMO) + 0.904 V.

Figure S1. Calibration of MMO in H$_2$ saturated 1M KOH.

Electrochemical impedance spectroscopy (EIS) measurements were carried out by applying an AC voltage with 5 mV amplitude in a frequency range from 100 KHz to 100 mHz at a potential of 1.518 V vs. RHE in 1 M KOH solution. The CV cycling test was conducted at a sweep rate of 50 mV s^{-1} from -0.46 V to 0.54 V vs MMO, and the resulting *i-v* curves were recorded at a sweep rate of 10 mV s^{-1} under 1 M KOH.

To study the electrocatalytic activity and stability, the polarization curves was tested from overpotential from 0 V to 1 V vs MMO at 10 mV/s. The chronoamperometry measurements were carried out at 20-200 mA cm^{-2} in the solution of 1.0 M KOH (pH=14). Prior to all experiments, the electrolyte solution was purged with high purity O$_2$ gas for 30 min. For comparison study, the electrocatalytic activities of NF and FeOOH NTAs-NF were also measured under the similar conditions. All electrochemical measurements were carried out at 25 °C. Unless specifically mentioned, the voltammograms were recorded without iR-correction.

Alkaline polymer electrolyte water electrolysis tests

Alkaline polymer electrolyte water electrolyzer (APEWE) cell experiments were performed by constructing an electrolysis cell (2×2.5 cm^2). To evaluate the OER performance of the prepared catalyst in real electrolysis, two APE water electrolysers were assembled.

Cell-1:

The prepared Ni$_{0.7}$Co$_{0.3}$O$_x$ loading was 2 mg cm^{-2} for the anode and 1 mg cm^{-2} (40 wt.% Pt/C, Johnson Matthey) for the cathode. A wet-proof carbon paper and a porous Ti plate were chosen as the cathode and anode diffusion layer, respectively. An AEH membrane (home-made) was chosen as the solid polymer electrolyte. To prepare a thin catalyst coated membrane (CCM) electrode, 5 wt% of AS-4 solution (0.6 mg cm^{-2}) and isopropanol were sprayed onto each side of membrane, followed by spaying the catalyst inks (1/3 of the

mass of catalyst). A Pt-plated porous Ti (0.7 mm in thickness) and wet-proof carbon paper were chosen as the anode and cathode diffusion layer, respectively. The catalyst coated membrane and a carbon paper were then hot-pressed at 60°C and 0.5 MPa for 1 min. The steady-state *i-V* tests were conducted at 60 °C in potentiostatic mode. The stability test was performed at 100 mA cm^{-2} and 60 °C, 1wt.% KOH solution was supplied to anode compartment at 5 mL min^{-1}.

Cell-2:

The commercial non-PGM OER catalysts (ATCA 3030, ACTA SPA corporation.) loading was 2 mg cm^{-2} for the anode, under the condition that other parameters were the same to Cell-1.
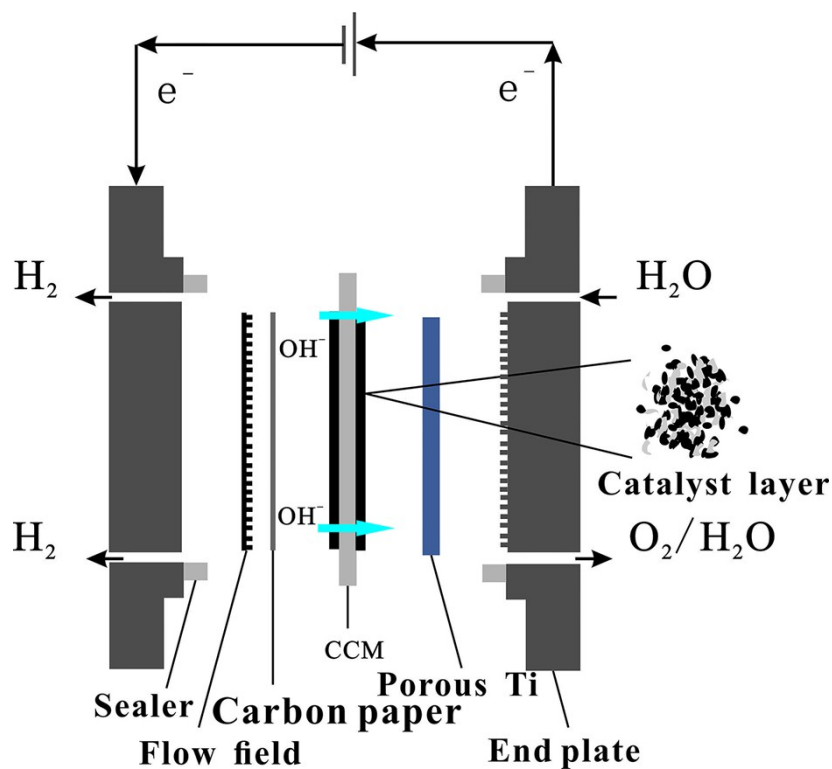

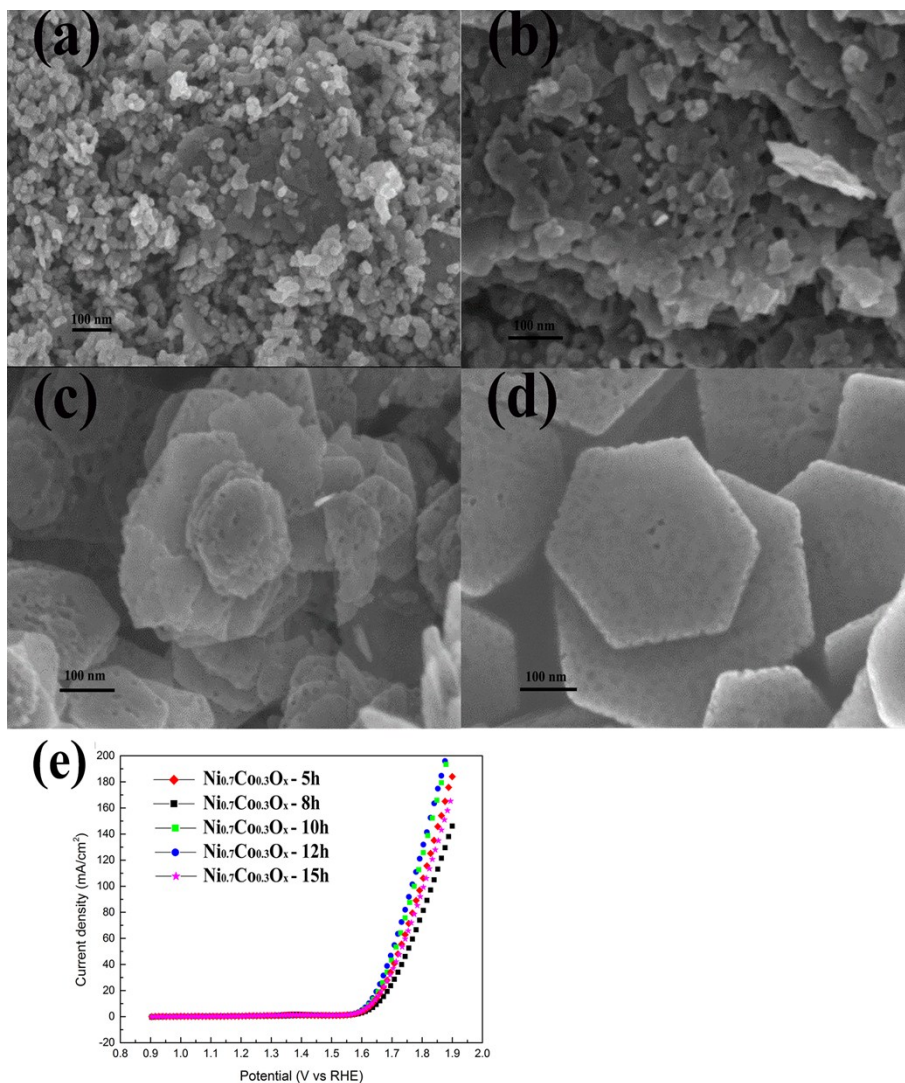**Fig. S1**. The schematic of APE cell structure.

Fig.S2 The SEM images of nickel/cobalt oxide synthesized with different reaction time, (a) 10 min, (b) 30 min, (c) 5 h, (d) 15 h; (e) LSV curves of the prepared $Ni_{0.7}Co_{0.3}O_x$ samples with different time in 1 M KOH at 10mV s^{-1} at 25°C.

Fig.S2a-d shows the SEM images of $Ni_{0.7}Co_{0.3}O_x$ OER electrocatalyst prepared with 10 min, 30 min, 5 h, and 15 h. At the very beginning of the reaction, small particles (ca. 20 nm in diameter) appeared. With reacting time extended, regular and uniform hexagon nano-plate (ca. 200 nm) in diameter was obtained. Fig.S2e shows the polarization curves of several samples prepared for 5 h, 8 h, 10 h, 12 h, and 15 h. The samples were remarked as $Ni_{0.7}Co_{0.3}O_x$-n, where n (5 h, 8 h, 10 h, 12 h, and 15 h) is reaction time. As revealed by the polarization curves, $Ni_{0.7}Co_{0.3}O_x$-12 h exhibits the best OER electrocatalytic activity, affording a current density of 10 mA cm^{-2} at a small overpotential of a mere 0.393 V in 1 M KOH solution (1.623 V vs. RHE)
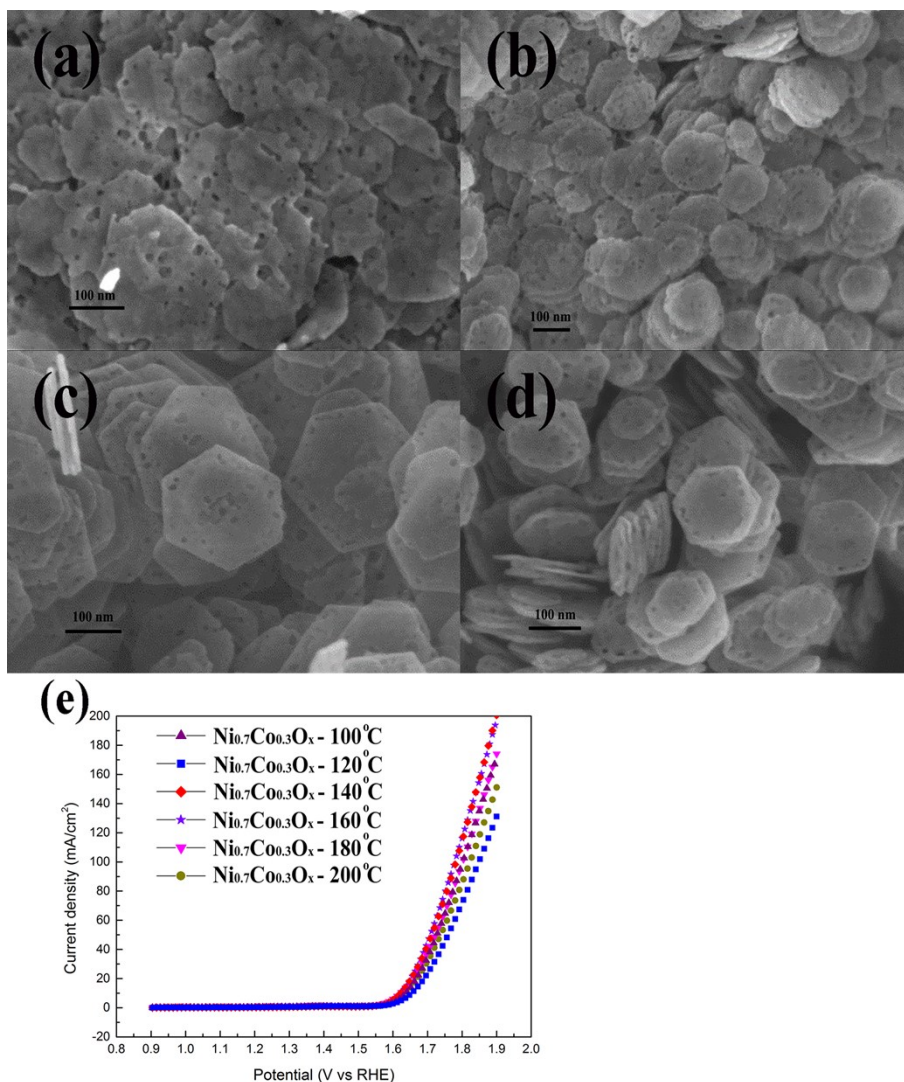
Fig.S3 The SEM images of nickel/cobalt oxide synthesized with different temperature, (a) 100 °C, (b) 140 °C, (c) 160 °C, (d) 180 °C，(e) LSV curves of the prepared $Ni_{0.7}Co_{0.3}O_x$ samples with different time in 1 M KOH at 10 mV s^{-1} at 25°C.

Fig.S3a-e shows the SEM images of $Ni_{0.7}Co_{0.3}O_x$-n, (n=100, 140, 160, and 180 °C) synthetized at different temperatures. When samples were prepared at low temperature (100, 120 °C), the edges of the prepared nano-plate were hackly. When temperature reached 160 oC, regular hexagon nano-plates (ca. 100 nm) were obtained. Furthermore, the morphology didn't change much as the temperature was elevated to 200 °C. As revealed by the i-V curves, $Ni_{0.7}Co_{0.3}O_x$-160 °C exhibits the best OER electrocatalytic activity, affording a current density of 10 mA cm^{-2} at a small overpotential of a mere 0.394 V in 1 M KOH solution (1.624 V vs. RHE).
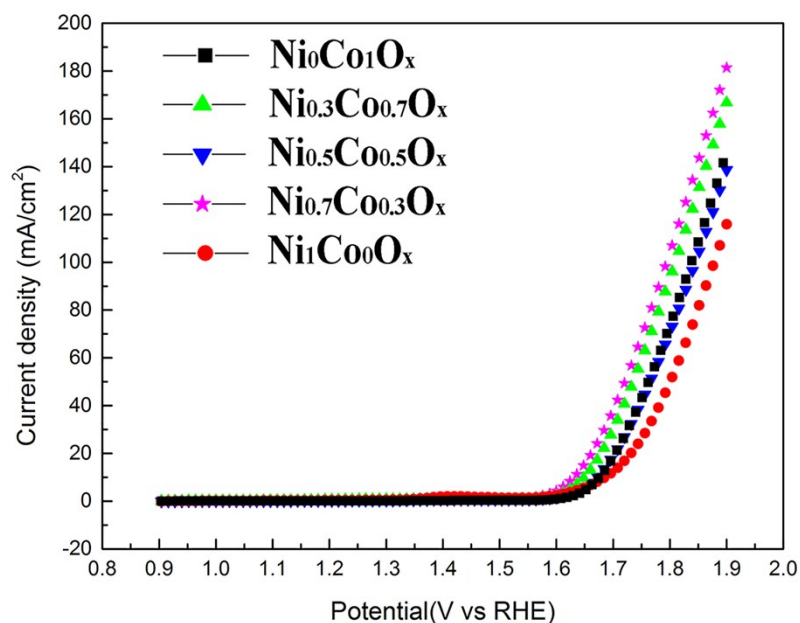
Fig.S4 The SEM images of nickel/cobalt oxide synthesized with different precursor contents, (a) CoO_x, (b) $Ni_{0.3}Co_{0.7}O_x$, (c) $Ni_{0.5}Co_{0.5}O_x$, (d) $Ni_{0.7}Co_{0.3}O_x$, (e) NiO_x , (e) LSV curves of images of nickel/cobalt oxide synthesized with different precursor content ratios in 1 M KOH at 10mV s^{-1} at 25°C.

Table. S1 Comparison of OER activity data for different catalysts.

Sample	Electrolyte	Overpotential (V)	Reference
NiCo film	0.5 M KOH	0.422V@ 75mA cm^{-2}	[2]
α-Ni(OH)$_2$ hollow sphere	0.1 M KOH	0.331V@ 10mA cm^{-2}	[3]
β-Ni(OH)$_2$ plates	1 M KOH	0.440V@ 10mA cm^{-2}	[3]
RuO_2	1 M KOH	0.387V@ 10mA cm^{-2}	[3]
RuO_2	1 M KOH	0.282V@ 10mA cm^{-2}	This work
IrO_2	1 M KOH	0.295V@ 10mA cm^{-2}	This work
$Ni_yFe_{1-y}O_x$/C particles	1 M KOH	0.280V@ 10mA cm^{-2}	[4]
$Ni_xCo_{1-x}(OH)_2$	1 M KOH	0.329V@ 5mA cm^{-2}	[5]
ZnCo(OH)$_x$/Graphene	0.1 M KOH	0.330V@ onset potential	[6]
$Ni_{0.7}Co_{0.3}O_x$	1 M KOH	0.394V@ 10mA cm^{-2}	This work

Table S2. APEWE single cell test.

Catalyst				Electrolyte	Performance	Stability	reference
Anode	Loading (mg cm^{-2})	Cathode	Loading (mg cm^{-2})				
Ni/Fe	~	Ni/Mo	~40	Deionized water	1.81V @400 mA cm^{-2}	8 h	[7]
NiFe(OH)$_2$	~	NiMo	~	4 M KOH	1.90 V @500 mA cm^{-2}	220 h	[8]
Cu$_{0.7}$Co$_{2.3}$O$_4$	~3	Ni	~2	Deionized water	2.24 V @500 mA cm^{-2}	None	[9]
Cu$_{0.6}$Mn$_{0.3}$Co$_{2.1}$O$_4$	~3	20wt.%Pt/C	~2	Deionized water	1.90 V @100 mA cm^{-2}	120 h	[10]
Ni$_{0.7}$Co$_{0.3}$O$_x$	~2	40wt.%Pt/C	~1	1 wt.% KHCO$_3$	2.00 V @100 mA cm^{-2}	550 h	This work

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