Electronic Supplementary Information

Experimental Section

Materials: $Ni(NO_3)_2·6H_2O$ and NaH_2PO_2 were purchased from Aladdin Ltd. in Shanghai. Hexamethylenetetramine (HMT) was purchased from Beijing Chemical Works. Nitric acid (HNO_3) and ethanol were purchased from Tianjin Chemical Corporation. $K_2B_4O_7·4H_2O$ was provided by Chengdu Kelong Chemical Reagent Factory. $RuCl_3·3H_2O$ and Nafion (5 wt%) were purchased from Sigma-Aldrich Chemical Reagent Co., Ltd. CC was provided by Hongshan District, Wuhan Instrument Surgical Instruments business, and was pretreated in HNO_3 and then cleaned by sonication in water and ethanol for several times to remove surface impurities. The water used throughout all experiments was purified through a Millipore system.

Preparation of Ni_2P/CC and Ni-Bi-Pi/CC: Ni_2P/CC was prepared as follows. In a typical synthesis, 1.4 g HMT and 1.45g $Ni(NO_3)_2.6H_2O$ were firstly dissolved in 36 mL ultrapure water under vigorous stirring for 10 min. Then the above pellucid solution and a piece of cleaned CC (2 cm × 3 cm) were transferred to a 50 mL Teflon-lined stainless-steel autoclave and maintained at 100 °C for 10 h. When the autoclave cooled down naturally, the resulting CC was taken out and washed with ultrapure water and dried at 60 °C. To obtain Ni_2P/CC, the resulting CC and NaH_2PO_2 (1 g) were placed at two separate positions in one closed porcelain crucible, and NaH_2PO_2 was located at the upstream side of the furnace. Then the sample were heated at 300 °C for 2.5 h with a heating speed of 1 °C min^{-1} in a static Ar atmosphere and cooled to ambient temperature under Ar. To achieve the preparation of Ni-Bi-Pi/CC, such Ni_2P/CC was activated with the potential of 1.1 V vs. Ag/AgCl in 0.1 M K-Bi at pH 9.2, and the current density continuously grows during activation process for about 2.5 h before achieving the top value.

Characterizations: XRD measurements were performed using a RigakuD/MAX 2550 diffractometer with Cu Kα radiation (λ=1.5418 Å). SEM images were collected on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. TEM measurements were made on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) with an accelerating voltage of 200 kV. XPS measurements were performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source. Inductively coupled plasma mass spectrometry (ICP-MS) analysis was performed on Thermo Scientific iCAP6300.

Electrochemical measurements: Electrochemical measurements were performed with a CHI 660E electrochemical analyzer (CH Instruments, Inc., Shanghai) in a standard three-electrode system using a Ni-Bi-Pi/CC as the working electrode, a platinum wire as the counter electrode and a Ag/AgCl as the reference electrode. The potentials reported in this work were calibrated to RHE other than especially explained, using the following equation: E (RHE) = E (Ag/AgCl) + (0.197 + 0.059 pH) V. Polarization curves were obtained by linear sweep voltammetry with a scan rate of 2 mV s^{-1}. All experiments were carried out at 25 °C.

Turnover frequency (TOF): The rough estimation of TOF for each active site makes it possible to compare the activity of Ni-Bi-Pi with that of other non-noble-metal catalysts. Herein, we attempt to use the following equation to calculate TOF value:

$$\mathrm{TOF} = I / (4\,F \times n)$$

Where I is current (A) at defined overpotential during the LSV measurement in 0.1 M K-Bi, and F is the Faradic constant (96485 C mol^{-1}), and n is the number of active sites, which is defined as the area of the oxidation peak of the Ni-Bi-Pi/CC at onset potential of 1.51 V as presented in Fig. 3a.

Determination of Faradaic efficiency (FE): The oxygen generated at anode was confirmed by gas chromatography (GC) analysis and measured quantitatively by using a calibrated pressure sensor to monitor the pressure change in the anode compartment of a H-type electrolytic cell. The FE was calculated by comparing the amount of experimentally measured oxygen generated by potentiostatic anodic electrolysis with theoretically calculated oxygen (assuming 100% FE). GC analysis was carried out on GC-2014C (Shimadzu Co.) with thermal conductivity detector and nitrogen carrier gas. Pressure data during electrolysis were recorded using a CEM DT-8890 Differential Air Pressure Gauge Manometer Data Logger Meter Tester with a sampling interval of 1 point per second.

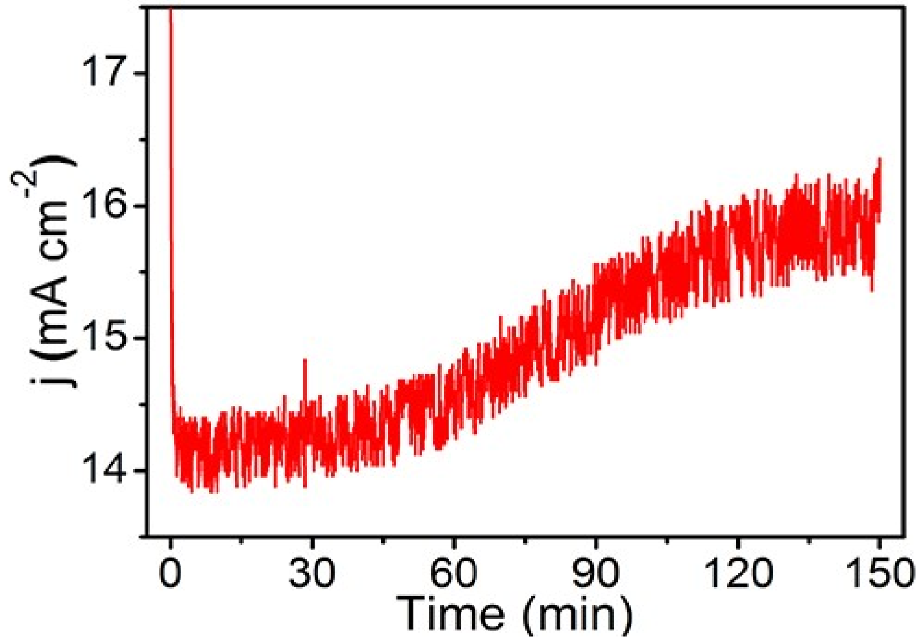

Fig. S1. Time-dependent current density curve for oxidative polarization.

Table S1. ICP-MS data for three Ni-Bi-Pi samples.

Catalyst	Ni (mg/cm^2)	B (mg/cm^2)	P (mg/cm^2)	O (mg/cm^2)	Ni/B/P/O atomic ratio
Sample 1	0.629	0.085	0.633	0.845	1.36:1.0:2.60:6.71
Sample 2	0.630	0.087	0.639	0.837	1.33:1.0:2.56:6.49
Sample 3	0.621	0.084	0.637	0.842	1.36:1.0:2.64:6.77
Average	0.627	0.085	0.636	0.841	1.34:1.0:2.60:6.66

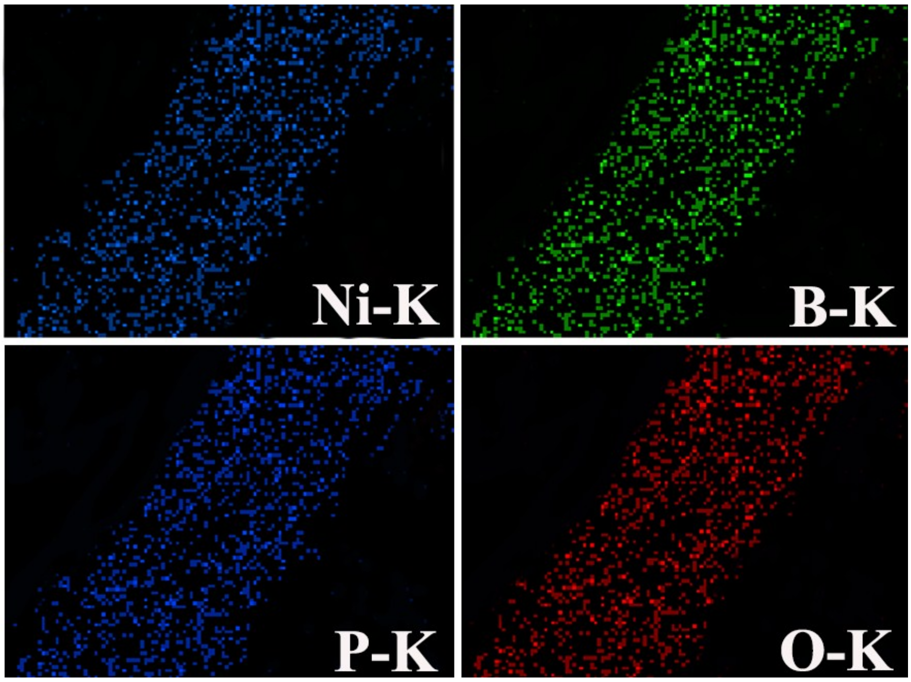

Fig. S2. The corresponding EDX elemental mapping images of Ni, B, P and O elements in Ni-Bi-Pi.

Table S2. Comparison of OER performance for Ni-Bi-Pi/CC with Ni-containing electrocatalysts under benign conditions.

Catalyst	**j (mA cm^{-2})**	**η (mV)**	**Electrolyte**	**Ref.**
Ni-Bi-Pi/CC	1	280	0.1 M K-Bi	This work
	5	302	0.1 M K-Bi	
	10	440	0.1 M K-Bi	
Ni-Bi film/FTO	1	540	0.5 M K-Bi	1
Ni-Bi film/ITO	1	~425	0.1 M Bi	2
Ni-Bi film/FTO	1	390	0.5 M K-Bi	3
Ni-Bi film/FTO	1	410	1 M K-Bi	4
Ni-Bi film/FTO	0.6	618	0.1 M Na-Bi	5
NiO$_x$-en/FTO	1	510	0.6 M Na-Bi	6
Ni-Ci/GC	1	517	0.2 M Ci	7
NiOx-MWCNT	0.5	330	0.1 M K-Bi	8
NiO$_x$-Bi	1	650	0.5 M K-Bi	9
NiO$_x$-Fe-Bi	5	552	0.5 M K-Bi	9
Ni-4Gly	1	480	0.25 M PBS	10
Co-Ni LDH/FTO	1	490	0.1 M K-Pi	11

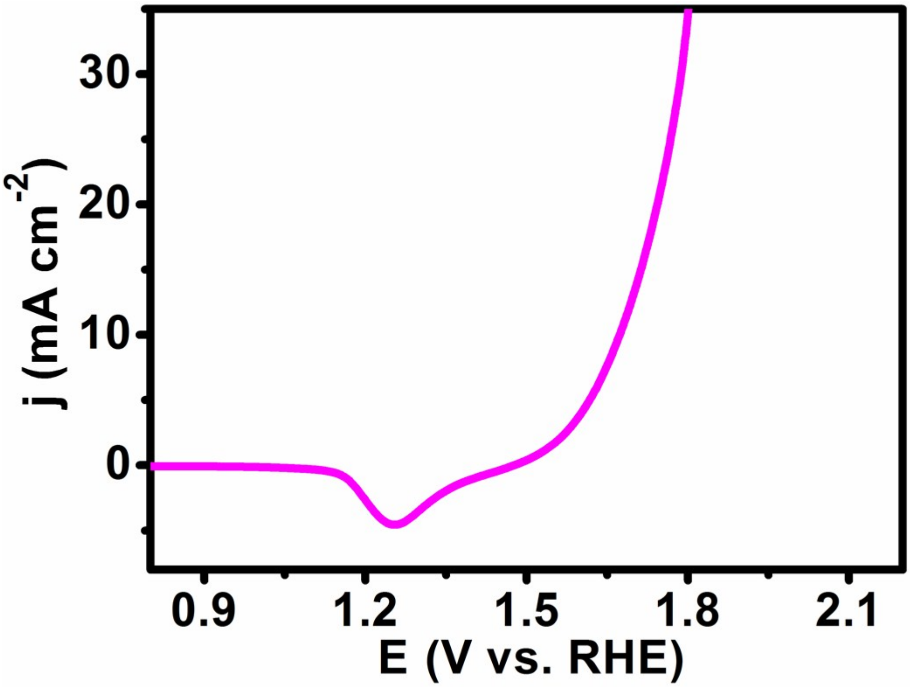

Fig. S3. LSV curve of Ni-Bi-Pi/CC for OER tested from high potential to low one in 0.1 M K-Bi.

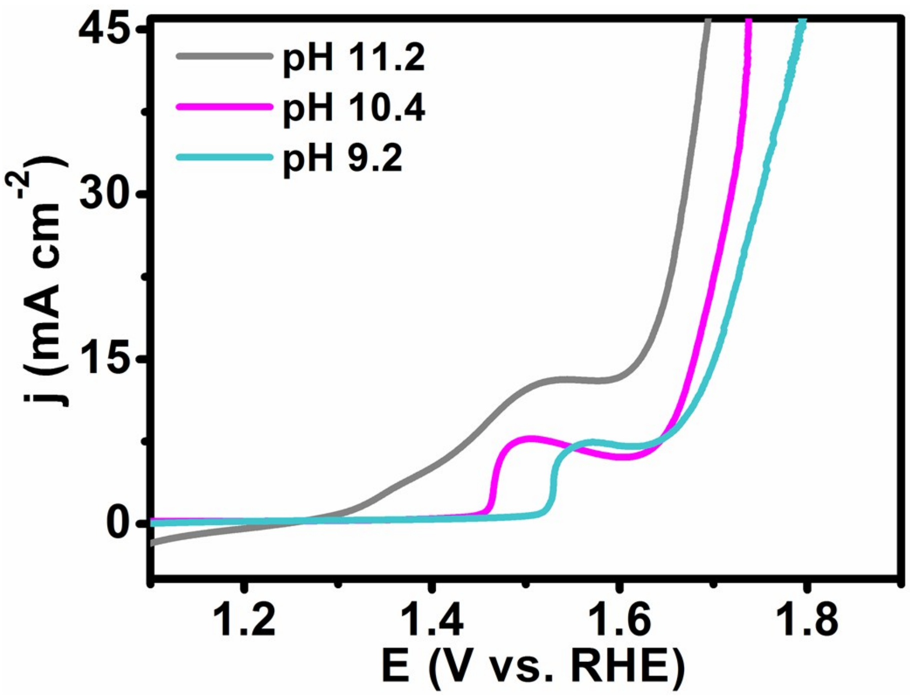

Fig. S4. The LSV curves of Ni-Bi-Pi/CC for OER in 0.1 M K-Bi under varied pH values.

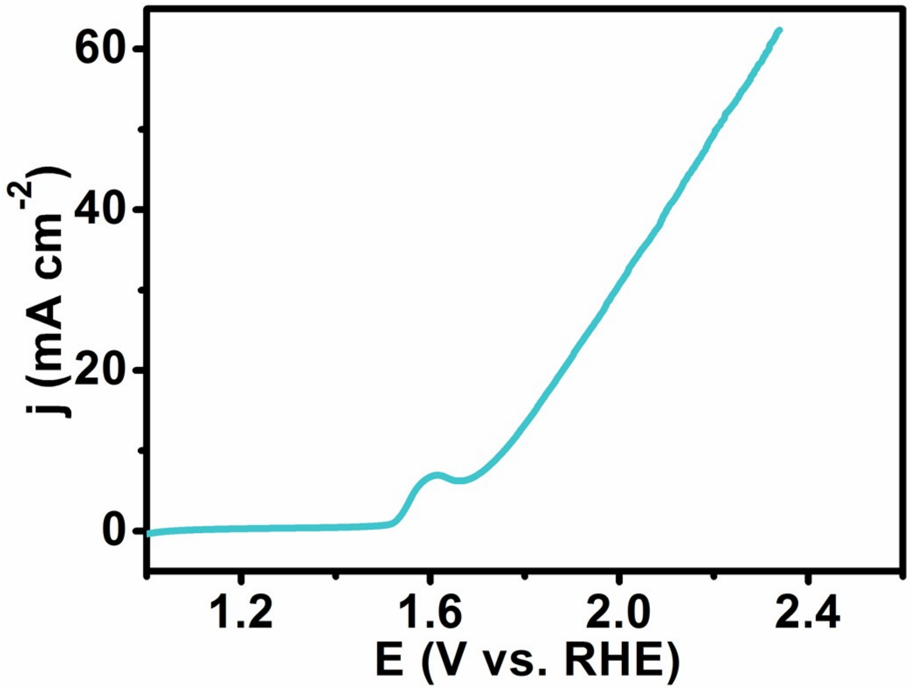

Fig. S5. Initial LSV curve for Ni-Bi-Pi/CC without iR correction in 0.1 M K-Bi.

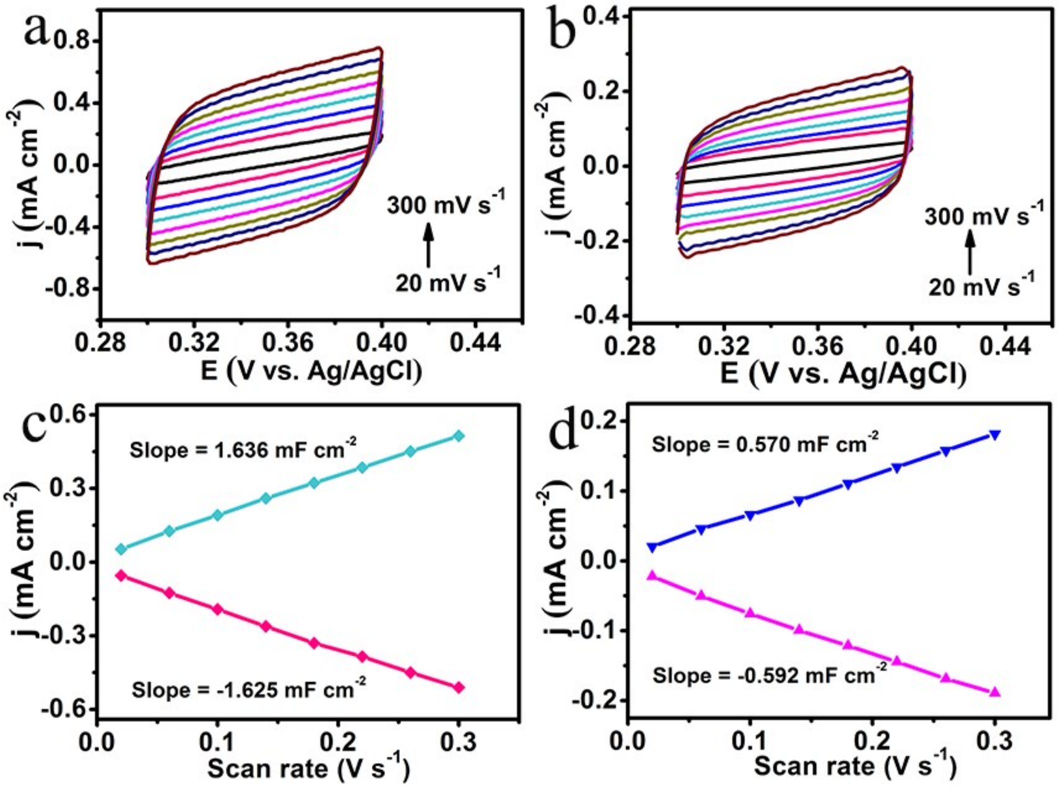

Fig. S6. CVs for (a) Ni-Bi-Pi/CC and (b) bare CC in the non-faradaic capacitance current range at scan rates of 20, 60, 100, 140, 180, 220, 260 and 300 mV s^{-1}. Corresponding capacitive currents at 0.35 V vs. Ag/AgCl as a function of scan rate for (c) Ni-Bi-Pi/CC and (d) bare CC in 0.1 M K-Bi. The determined double-layer capacitance of the system is taken as the average of the absolute value of the slope for the linear fitting to the data.

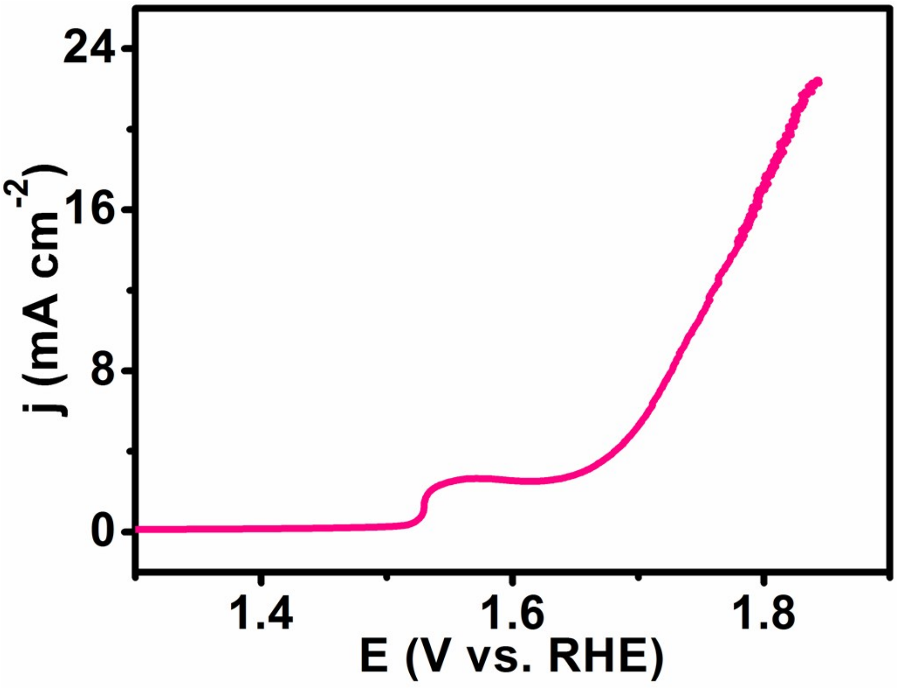

Fig. S7. LSV curve normalized by ECSA for Ni-Bi-Pi/CC in 0.1 M K-Bi.

References

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