Electronic Supplementary Information

Experimental Section

Materials: CC was bought from Hongshan District, Wuhan Instrument Surgical Instruments business, and treated in nitric acid (HNO₃) to serve as substrate for active materials. Ni(NO₃)₂·6H₂O were purchased from Aladdin Ltd. in Shanghai. Hexamethylenetetramine (HMT) was provided by Beijing Chemical Works. HNO₃ and ethanol were purchased from Tianjin Chemical Corporation. K₂B₄O₇·4H₂O was purchased by Chengdu Kelon Chemical Reagent Factory. RuCl₃·3H₂O and Nafion (5 wt%) were bought from Sigma-Aldrich Chemical Reagent Co., Ltd. All chemical regents were used as received without further purification. Deionized water was made by the Millipore system and used in all experimental process.

Preparation of NiO/CC and Ni-Bi/CC: Typically, CC was first treated with concentrated HNO₃, ethanol and deionized water by sonication to achieve a clean surface before use. Then CC was put into deionized water (36 ml) containing Ni(NO₃)₂·6H₂O (1.45 g) and HMT (1.4 g). After vigorous stirring for several minutes, the aqueous solution and CC were transferred to a 50 ml Teflon-lined stainless-steel autoclave. It was heated at 100 °C for 10 h to achieve Ni(OH)₂/CC. The resulting Ni(OH)₂/CC was washed with deionized water for several times and further annealed at 300 °C in Ar atmosphere to convert into NiO/CC. To realize the transformation of NiO/CC to Ni-Bi/CC, NiO/CC was used as the working electrode in a three-electrode setup with the potential of 0.9 V *vs.* Ag/AgCl in 0.1 M K-Bi (pH 9.2). After 12 h operating, the current density reaches a top value, indicating the successful synthesis of Ni-Bi/CC.

Synthesis of RuO₂: RuO₂ was prepared in accordance with previous report.¹ Firstly, 2.61 g RuCl₃· $3H_2O$ was dispersed in 100 mL distilled water and stirred for 10 minutes at 100 °C. Then 1.0 ml NaOH (1.0 M) was added into the above solution. And the mixture was under 100 °C for another 45 minutes. After cool to room temperature, the mixture

was centrifuged to collect the precipitation, further dried at 80 °C for 12 h. The dried precipitation was annealed at 300 °C in Ar atomosphere to achieve RuO₂.

Characterizations: XRD measurements were performed using a RigakuD/MAX 2550 diffractometer with Cu K α 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.

Electrochemical measurements: Electrochemical measurements were performed with a CHI 660E electrochemical analyzer (CH Instruments, Inc., Shanghai). In a typical three-electrode system, the Ni-Bi/CC was used as the working electrode, a platinum wire as the counter electrode and Ag/AgCl as the reference electrode. The potentials reported in this work were converted to the RHE with the following equation: E (RHE) = E (Ag/AgCl) + (0.197 + 0.059 pH) V. Linear sweep voltammetry test was performed at a scan rate of 1 mV s⁻¹ between 0.2 and 1.7 V (*vs.* Ag/AgCl) at room temperature. To calculate turnover frequency, cyclic voltammetry (CV) tests of Ni-Bi/CC were conducted from 0.5 and 1 V (*vs.* Ag/AgCl), with scanning rates of 5, 10, 15, 20, 25 mV s⁻¹, respectively.

TOF calculation: TO calculate TOF, the surface concentration of active sites related to the redox Ni species was first obtained. According to the electrochemical CV curves (Fig. S4a), the oxidation peak current of redox species presents linear change on scan rates (Fig. S4b). The slope of the line can be calculated using the following equation:

$$slope = \frac{n^2 F^2 A \tau_0}{4RT}$$

n is the number of electrons transferred, F is Faraday's constant, A is the surface area of the electrode, τ_0 is the surface concentration of active sites (mol cm⁻²), and R and T are the ideal gas constant and the absolute temperature, respectively. TOF values can be

finally calculated based on the formula:

$$TOF = \frac{JA}{4FM}$$

J is the current density at certain overpotential, A is the area of the electrode, 4 indicates the mole of electrons consumed for evolving one mole of O_2 from water, F is Faraday's constant and m is the number of moles for active sites.

Determination of FE: FE was calculated by comparing the amount of experimentally quantified gas with theoretically calculated gas. The experimentally evolved gas was confirmed by gas chromatography (GC) analysis and measured quantitatively by monitoring the pressure change via a calibrated pressure sensor in the anode compartment of a H-type electrolytic cell. The number of theoretically evolved gas was calculated by presuming that all charges through the anode were 4e⁻ oxidation for oxygen production.



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



Fig. S2. Cross-sectional SEM image of Ni-Bi/CC.



Fig. S3. (a) The SEM image for Ni-Bi/CC. The corresponding EDX elemental mapping images of Ni (b), B (c) and O (d) elements for Ni-Bi/CC.



Fig. S4. (a) Cyclic voltammogram curves of Ni-Bi/CC under different scan rate tested in 0.1 M K-Bi. (b) Linear relationship of the peak current of Ni^{3+}/Ni^{4+} oxidation wave with the scan rate.



Fig. S5. SEM images for the post-catalysis Ni-Bi/CC under different magnification.

Catalyst	j (mA cm ⁻²)	η (mV)	Electrolyte	Ref.
Ni-Bi/CC	10	470	0.1 M K-Bi	This work
	10	390	0.5 M K-Bi	
Ni-Bi film/FTO	1	670	1 M K-Bi	2
Ni-Bi film/ITO	1	425	0.1 M Bi	3
Ni-Bi film/FTO	1	390	0.5 M K-Bi	4
Ni-Bi film/FTO	1	540	0.5 M K-Bi	5
Ni-Bi film/FTO	1.5	610	0.1 M Na-Bi	6
NiO _x -Fe-Bi	5	522	0.5 M K-Bi	7
NiO _x -Bi	1	560	0.5 M K-Bi	7
Co-Pi/Ni foam	100	363	1 M K-Bi	8
Ni-Ci/GC	1	517	0.2 M Ci	9
NiOx-MWCNT	0.5	330	0.1 M K-Bi	10
NiO _x -en/FTO	1	510	0.6 M Na-Bi	11
Ni-4Gly	1	480	0.25 M PBS	12

Table S1. Comparison of catalytic performance for Ni-Bi/CC with other Ni-based OER
 electrocatalysts under benign conditions.

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