## **Electronic Supplementary Information**

## **Experimental section**

**Materials:** Carbon Cloth (CC) was provided by Hongshan District, Wuhan Instrument Surgical Instruments business, and treated in nitric acid (HNO<sub>3</sub>) to serve as substrate for active materials. Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O were purchased from Aladdin Ltd. in Shanghai. Hexamethylenetetramine (HMT) was provided by Beijing Chemical Works. HNO<sub>3</sub> and ethanol were purchased from Tianjin Chemical Corporation. Potassium bicarbonate (KHCO<sub>3</sub>) was purchased by Chengdu Kelon Chemical Reagent Factory. RuCl<sub>3</sub>·3H<sub>2</sub>O and Nafion (5 wt%) were bought from Sigma-Aldrich Chemical Reagent Co., Ltd. All chemical regents were used as received without further purification. The water used throughout all experiments was purified through a Millipore system.

**Preparation of NiO/CC:** NiO/CC was prepared as follows. In a typical synthesis, a piece of CC was first treated with concentrated HNO<sub>3</sub>, ethanol and deionized water by sonication sequentially to obtain a clean surface before use. To prepare Ni(OH)<sub>2</sub> precursor using a hydrothermal reaction, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (1.45 g) and HMT (1.4 g) were dissolved in 36 mL water under vigorous stirring for 30 min. Then the solution was transferred to a 50 mL Teflon-lined stainless-steel autoclave in which a piece of CC was immersed into the solution. The autoclave was sealed and maintained at 100 °C for 10 h in an electric oven to obtain Ni(OH)<sub>2</sub> precursor. After the autoclave cooled down to room temperature, the CC covered with Ni(OH)<sub>2</sub> nanosheet array was taken out and washed with water and ethanol for several times, followed by drying at 60 °C for 2 h, and then annealed at 350 °C in air for 2 h with a heating rate of 5 °C min<sup>-1</sup> to obtain NiO/CC.

**Preparation of NiO@Ni-Ci/CC:** We prepared NiO@Ni-Ci/CC via oxidative polarization of NiO/CC for 2 h at 1.0 V vs. Ag/AgCl in 1.0 M K-Ci (pH 8.3) at room temperature (25 °C). NiO/CC, Ag/AgCl and graphite plate were used as the working electrode, reference electrode and counter electrode, respectively. The loading of asprepared NiO@Ni-Ci was determined to be 1.8 mg cm<sup>-2</sup> using a high precision microbalance.

Synthesis of RuO<sub>2</sub>: RuO<sub>2</sub> was prepared in accordance with reported work.<sup>1</sup> Briefly, 2.61 g of RuCl<sub>3</sub>·3H<sub>2</sub>O and 1.0 mL KOH (1.0 M) were added into 100 mL distilled water and stirred for 45 min at 100 °C. Then the above solution was centrifuged for 10 minutes and filtered. The precipitates were collected by centrifugation and washed with water for several times, followed by drying at 70°C. Finally, the product was annealed at 300°C for 3 h under air atmosphere. RuO<sub>2</sub> ink was prepared by dispersing 20 mg of catalyst into 490 µL of water/ethanol (v/v = 1:1) and 10 µL of 5 wt% Nafion using sonication for 30 min. Then 11.3 µL of the RuO<sub>2</sub> ink (containing 452 µg of RuO<sub>2</sub>) was loaded onto a bare CC of 0.25 cm<sup>-2</sup> in geometric area (loading: 1.8 mg cm<sup>-2</sup>).

**Characterizations:** Powder X-ray diffraction (XRD) patterns were performed using a RigakuD/MAX 2550 diffractometer with Cu K $\alpha$  radiation ( $\lambda$ =1.5418 Å). Scanning electron microscope (SEM) measurements were recorded on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. The structures of the samples were determined by transmission electron microscopy (TEM) images collected on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) operated at 200 kV. X-ray photoelectron spectroscopy (XPS) data of the samples was collected 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 standard three-electrode system. NiO@Ni-Ci/CC was used as the working electrode. A graphite plate and an Ag/AgCl were used as the counter electrode and the reference electrode, respectively. The temperature of solution was kept at 25 °C for all the measurements via the adjustment of air condition and heating support, which ensured the variation of diffusion coefficient below 1%. 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.



Fig. S1. EDX spectrum of NiO@Ni-Ci/CC.



Fig. S2. XPS spectra of NiO in the (a) Ni 2p and (b) O 1s regions.



Fig. S3. LSV curves for NiO/CC and NiO@Ni-Ci/CC in 1.0 M KOH for water oxidation.



**Fig. S4.** (a) LSV curves and (b) corresponding Tafel plots for NiO@Ni-Ci/CC in 0.2, 0.5 and 1.0 M K-Ci for water oxidation.



Fig. S5. LSV curves recorded for NiO@Ni-Ci/CC before and after 500 cyclic voltammetry cycles in 1.0 M K-Ci.



**Fig. S6.** (a) XRD pattern and (b) SEM image for NiO@Ni-Ci/CC after 500 cyclic voltammetry cycles.



**Fig. S7.** CVs for (a) NiO@Ni-Ci/CC and (b) NiO/CC in the non-faradaic capacitance current range at scan rates of 50, 100, 150, 200, 250, and 300 mV s<sup>-1</sup>. Corresponding capacitive currents at 0.07 V vs. Ag/AgCl as a function of scan rates for (c) NiO@Ni-Ci/CC and (d) NiO/CC in 1.0 M K-Ci.



**Fig. S8.** Nyquist plots for NiO/CC and NiO@Ni-Ci/CC in the frequency range from 0.01 to 10<sup>6</sup> Hz in 1.0 M K-Ci.



**Fig. S9.** The amount of oxygen theoretically calculated and experimentally measured vs. time for NiO@Ni-Ci/CC in 1.0 M K-Ci.

Catalyst	j (mA cm <sup>-2</sup> )	η (mV)	Electrolyte	Ref.
NiO@Ni-Ci/CC	15	560	0.2 M K-Ci	This work
	15	442	0.5 M K-Ci	
	15	387	1.0 M K-Ci	
	20	416	1.0 M K-Ci	
Fe-Ci/FTO	10	560	0.2 M Ci	2
NiOx-Cat/GC	1.15	~604	0.2 M K-Ci	3
Co-Ci/GC	9.1	~771	0.2 M K-Ci	4
Ni-Bi film/ITO	1.0	425	0.1 M Bi	5
Ni-Bi film/FTO	1.0	390	0.5 M K-Bi	6
Ni-Bi film/FTO	1.0	413	1.0 M K-Bi	7
Ni-Bi film/FTO	0.6	618	0.1 M Na-Bi	8
NiO <sub>x</sub> -en/FTO	1.0	510	0.6 M Na-Bi	9
NiO <sub>x</sub> -Bi	1.0	650	0.5 M K-Bi	10
CuO/FTO	0.1	430	0.1 M K-Bi	11
Ni-4Gly	1.0	480	0.25 M PBS	12
Fe-Bi/ITO	10	600	0.5 M BBS	13
Co-Ni LDH/FTO	1.0	490	0.1 M K-Pi	14
Cu-Bi/FTO	1.0	~525	0.2 M Na-Bi	15
Co-Pi NA/Ti	10	450	0.1 M K-Pi	16
Ni-Bi/CC	10	470	0.1 M K-Bi	17
NiS <sub>2</sub> @Ni-Bi/CC	15	455	0.1 M K-Bi	18
Fe-Co <sub>3</sub> O <sub>4</sub> @Fe-Co- Bi/CC	10	420	0.1 M K-Bi	19
CoP@Co-Bi-Pi/Ti	10	410	0.1 M K-Bi	20
Fe-Pi-Bi/CC	10	434	0.1 M K-Bi	21

 Table S1. Comparison of catalytic performance for NiO@Ni-Ci/CC with other

 reported non-noble-metal WOCs under benign conditions.

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