Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Experimental section

Materials: $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, NH_4F, and urea were purchased from Beijing Chemical Corp. The $RuCl_3 \cdot 3H_2O$ and Nafion (5 wt%) were purchased from Sigma-Aldrich Chemical Reagent Co., Ltd. Nitric acid (HNO_3) and ethanol were purchased from Tianjin Chemical Corporation. Carbon cloth (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 to remove surface impurities. The water used throughout all experiments was purified through a Millipore system.

Preparation of $NiCo_2O_4$/CC: To prepare the precursor of $NiCo_2O_4$/CC, $NiCl_2 \cdot 6H_2O$ (4 mmol), $CoCl_2 \cdot 6H_2O$ (8 mmol) and urea (15 mmol) were dissolved in 75 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 120 °C for 6 h in an electric oven. After the autoclave cooled down to room temperature, the precursor was taken out and washed with water and ethanol for several times, followed by drying at 60 ºC for 2 h. To prepare $NiCo_2O_4$/CC, the precursor was annealed at 450 °C in air for 2 h.

Preparation of $NiCo_2O_4$@Ni-Co-Ci/CC: The $NiCo_2O_4$@Ni-Co-Ci/CC was prepared by oxidative polarization of $NiCo_2O_4$/CC at a constant potential of 0.98 V vs. Ag/AgCl for 2.5 h. Two control samples were prepared by oxidative polarization at 1.08 V for 2.5 h and at 0.98 V for 20 h, respectively. The $NiCo_2O_4$/CC, Ag/AgCl and graphite plate were used as the working electrode, reference electrode and counter electrode, respectively. And 1.0 M K-Ci (pH: 8.3) was used as electrolyte. The $NiCo_2O_4$@Ni-Co-Ci loading was determined to be 1.7 mg cm^{-2} using a high precision microbalance.

Preparation of RuO_2/CC: RuO_2 was prepared according to reported method.[1] Briefly, 2.61 g $RuCl_3 \cdot 3H_2O$ and 30 mL NaOH (1.0 M) were added into 100 mL distilled water and stirred for 45 minutes at 100 °C. 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_2 ink was prepared by dispersing 20 mg of RuO_2 powder into 490 μL of water/ethanol (v/v = 1:1) solvent containing 10 μL of 5 wt% Nafion and sonicated for 30 min. Then the RuO_2 ink was coated onto a bare CC of 0.25 cm^{-2}.

Characterizations: The X-ray diffraction (XRD) patterns were collected by RigakuD/MAX 2550 diffractometer with Cu Kα radiation (λ = 1.5418 Å). The scanning electron microscopy (SEM) images were taken by a Hitachi S-4800 field emission scanning electron microscope at an accelerating voltage of 20 kV. The high-resolution transmission electron microscopy (HRTEM) measurements were performed on a Hitachi H-8100 electron microscopy with an accelerating voltage of 200 kV. The XPS scans were collected with a Thermal ESCALAB 250 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. $NiCo_2O_4$@Ni-Co-Ci/CC was used as the working electrode. A graphite plate and an Ag/AgCl electrode were used as the counter electrode and the reference electrode, respectively. The current densities were calculated with respect to the geometrical area of the electrodes (0.5 cm × 0.5 cm). The reference electrode was calibrated to the reversible hydrogen electrode (RHE) scale in all measurements using the following equation: E (RHE) = E (Ag/AgCl) + (0.197 + 0.059 pH) V. For Linear sweep voltammetry (LSV) measurements, the scan rate was set to be 5 mV s^{-1}. All experiments were carried out at 25 °C.

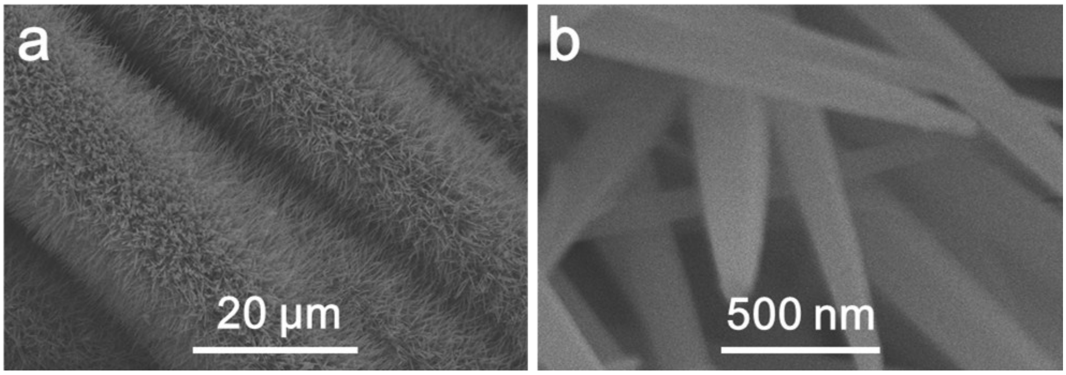

Fig. S1. Scanning electron microscopy images for the precursor of $NiCo_2O_4$/CC.

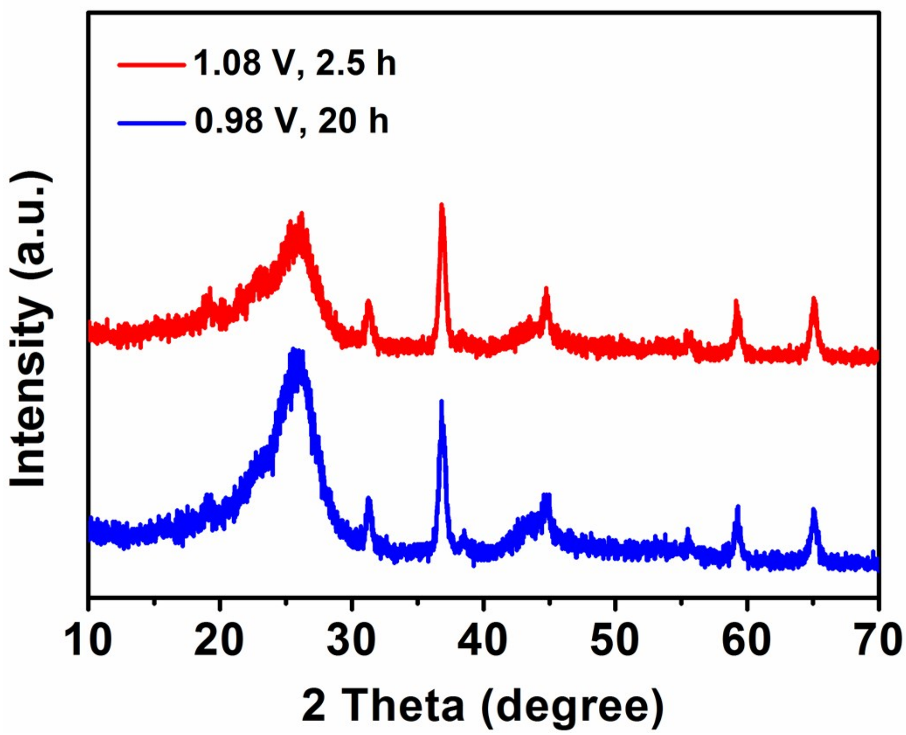

Fig. S2. XRD patterns of two control samples. Red curve: $NiCo_2O_4$/CC treated by oxidative polarization at 1.08 V for 2.5 h. Blue curve: $NiCo_2O_4$/CC treated by oxidative polarization at 0.98 V for 20 h.

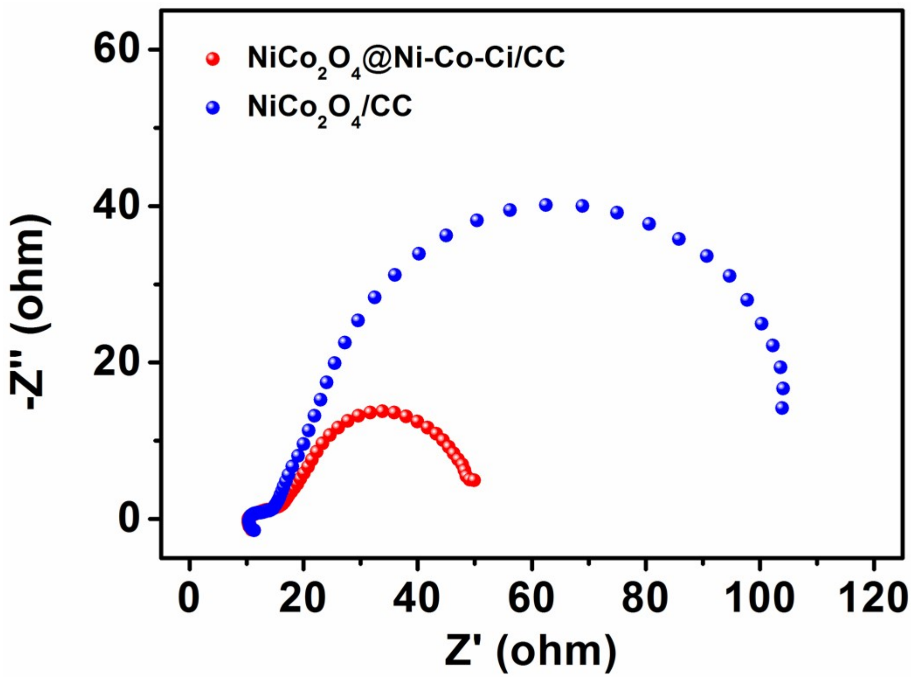

Fig. S3. The Nyquist plots for $NiCo_2O_4$@Ni-Co-Ci/CC and $NiCo_2O_4$/CC in 1.0 M K-Ci. These plots were collected at 0.85V (vs. Ag/AgCl) with a frequency range from 100000 to 0.1 Hz and an amplitude of 5 mV.

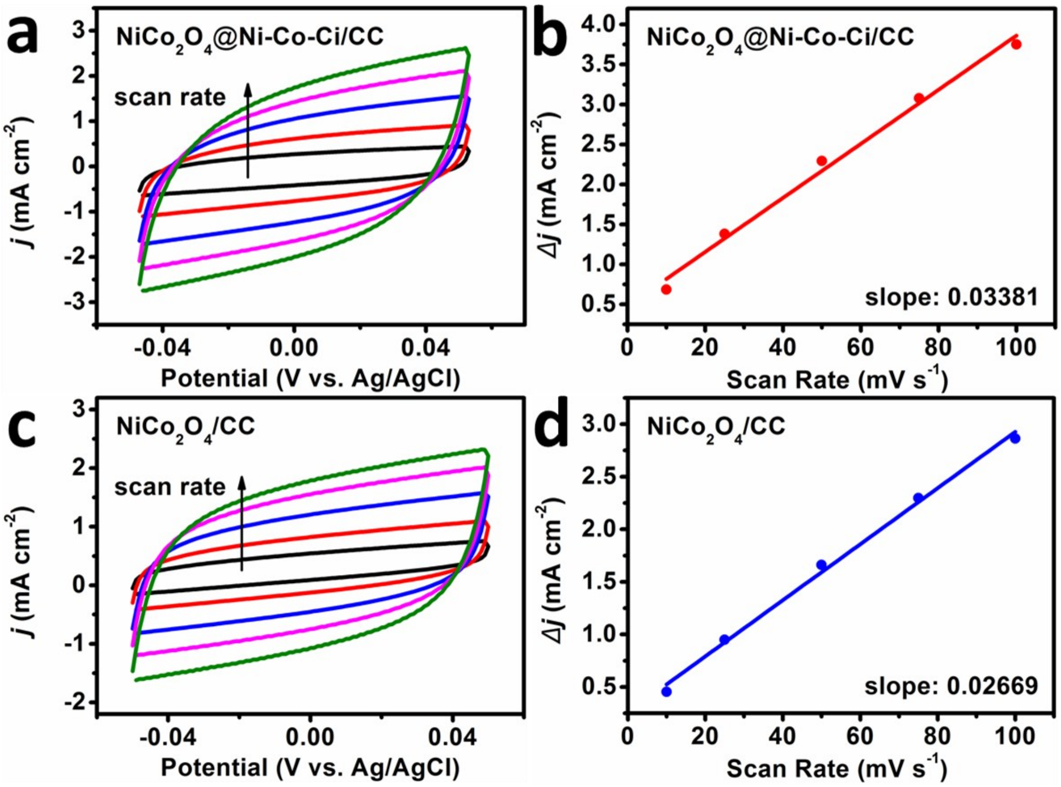

Fig. S4. Cyclic voltammograms collected at various scan rates (10, 25, 50, 75 and 100 mV s^{-1}) for (a) $NiCo_2O_4$@Ni-Co-Ci/CC and (c) $NiCo_2O_4$/CC in 1.0 M K-Ci. The difference (*Δj*) between capacitive currents as a function of scan rates for (b) $NiCo_2O_4$@Ni-Co-Ci/CC and (d) $NiCo_2O_4$/CC in 1.0 M K-Ci. The slope is twice of double layer capacitance.

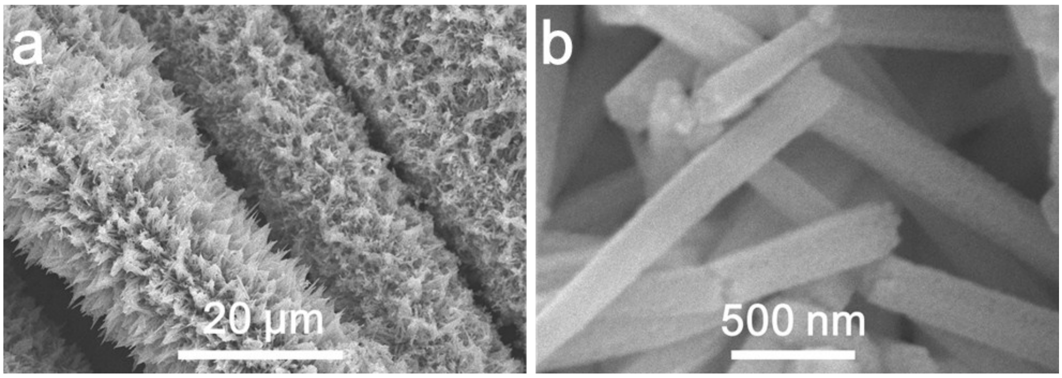

Fig. S5. SEM images of $NiCo_2O_4$@Ni-Co-Ci/CC after CV test.

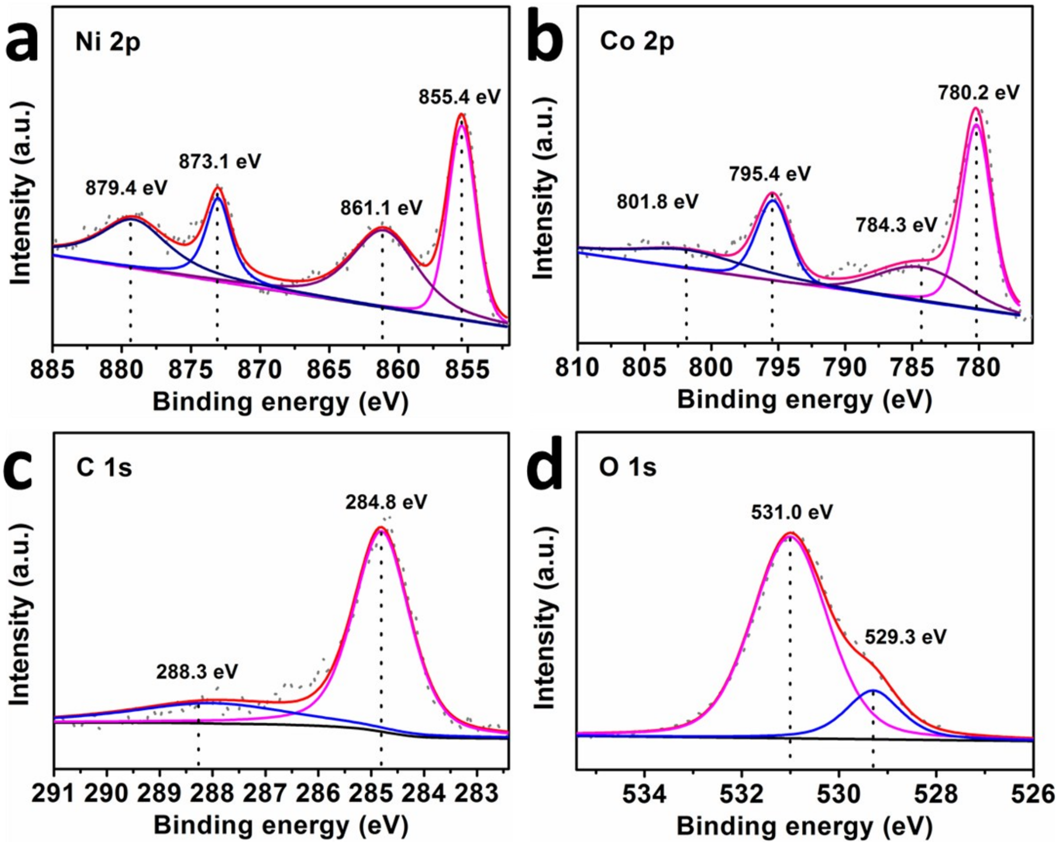

Fig. S6. XPS spectra of $NiCo_2O_4$@Ni-Co-Ci after CV test in the (a) Ni 2p, (b) Co 2p, (c) C 1s and (d) O 1s regions.

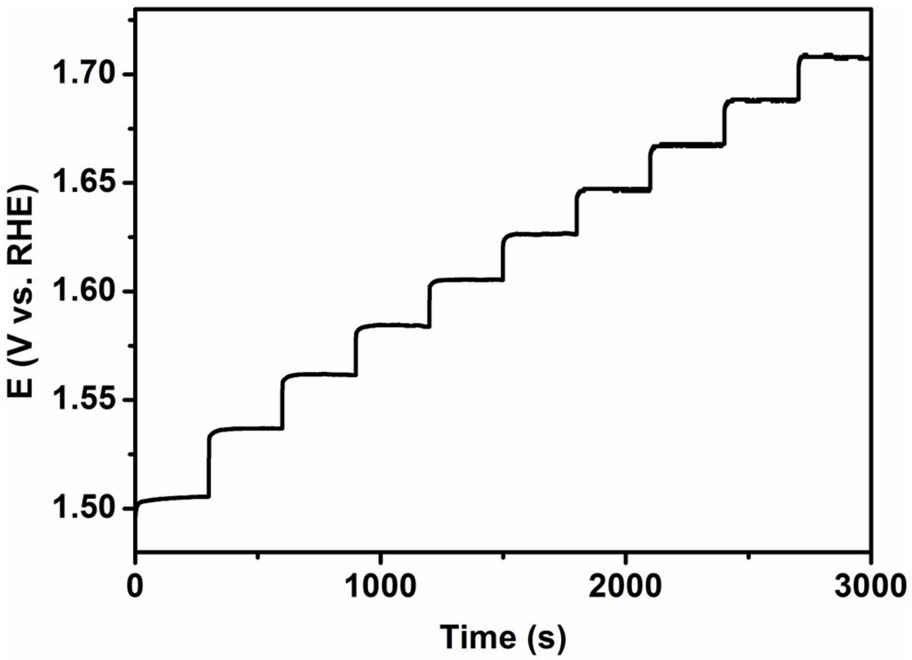

Fig. S7. Multi-current process of $NiCo_2O_4$@Ni-Co-Ci/CC. The current density started at 4 mA cm^{-2} and ended at 40 mA cm^{-2}, with an increment of 4 mA cm^{-2} per 300 s without iR correction.

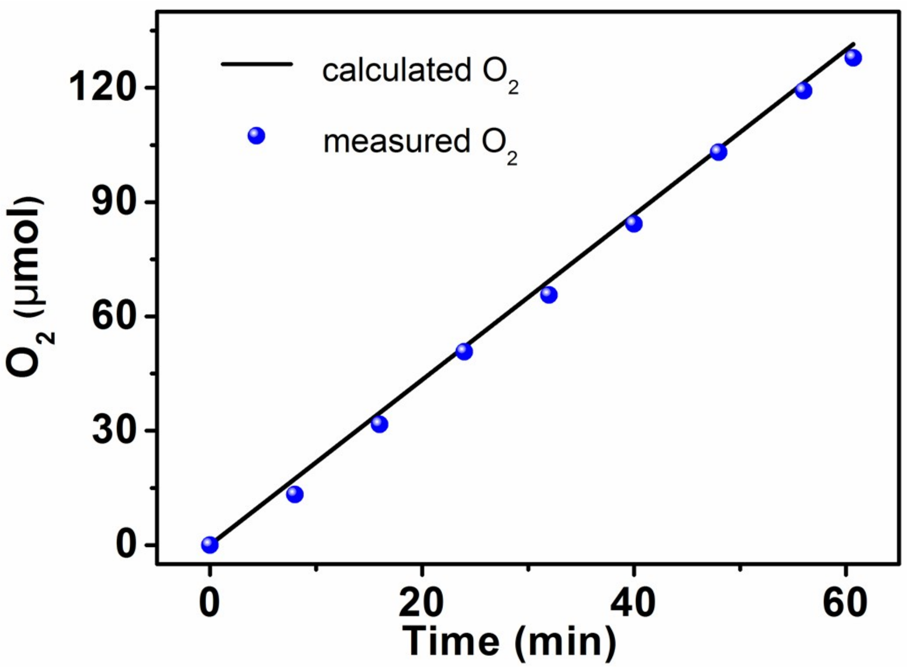

Fig. S8. Practically generated and theoretically calculated oxygen amount versus time for $NiCo_2O_4$@Ni-Co-Ci/CC in 1.0 M K-Ci.

Table S1. Comparison of catalytic performance for $NiCo_2O_4$@Ni-Co-Ci/CC with other reported non-noble-metal electrocatalysts under benign conditions.

Catalyst	j (mA cm^{-2})	η (mV)	Electrolyte	Ref.
$NiCo_2O_4$@Ni-Co-Ci/CC	10	507	0.2 M K-Ci	This work
	20	608	0.2 M K-Ci	
	20	503	0.5 M K-Ci	
	20	337	1.0 M K-Ci	
Fe-Ci/FTO	10	560	0.2 M Ci	2
Fe-Bi/ITO	10	600	0.5 M BBS	3
Co-Pi NA/Ti	10	450	0.1 M K-Pi	4
Co-Ci/GC	9.1	~771	0.2 M K-Ci	5
CoP@Co-Bi-Pi/Ti	10	410	0.1 M K-Bi	6
Fe-Co_3O_4@Fe-Co-Bi/CC	10	420	0.1 M K-Bi	7
Co-Ni LDH/FTO	1.0	490	0.1 M K-Pi	8
NiO_x-Cat/GC	1.15	~604	0.2 M K-Ci	9
Ni-Bi film/FTO	1.0	390	0.5 M K-Bi	10
Ni-Bi film/FTO	1.0	413	1.0 M K-Bi	11
Ni-Bi film/FTO	0.6	618	0.1 M Na-Bi	12
NiO_x-en/FTO	1.0	510	0.6 M Na-Bi	13
NiO_x-Bi	1.0	650	0.5 M K-Bi	14
Ni-Bi/CC	10	470	0.1 M K-Bi	15
Ni-4Gly	1.0	480	0.25 M PBS	16
CuO/FTO	0.1	430	0.1 M K-Bi	17
Cu-Bi/FTO	1.0	~525	0.2 M Na-Bi	18

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