

Electronic Supplementary Material

Nickel-carbonate nanowire array: An efficient and durable electrocatalyst for water oxidation under nearly neutral conditions

Yuyao Ji¹, Min Ma², Xuqiang Ji², Xiaoli Xiong (✉)^{1,3}, Xuping Sun (✉)²

1 College of Chemistry and Materials Science, Sichuan Normal University, Chengdu 610068, China

2 College of Chemistry, Sichuan University, Chengdu 610064, China

3 Key Lab of Process Analysis and Control of Sichuan Universities, Yibin University, Yibin 44000, China

© Higher Education Press and Springer-Verlag Berlin Heidelberg, part of Springer Nature 2018

E-mails: xionxiaoli2000@163.com (Xiong X); sunxp@scu.edu.cn (Sun X)

1.1 Materials

NF was provided by Hongshan District, Wuhan Instrument Surgical Instruments business, and treated in hydrochloric acid (HCl) to serve as substrate for active materials. Ni(NO₃)₂·6H₂O was purchased from Aladdin Ltd. in Shanghai. Ethanediamine and ethylene glycol were provided by Beijing Chemical Works. HCl and ethanol were purchased from Tianjin Chemical Corporation. Potassium bicarbonate (KHCO₃) 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 reagents were used as received without further purification. The water used throughout all experiments was purified through a Millipore system.

1.2 Characterizations

Powder X-ray diffraction (XRD) patterns were performed using a RigakuD/MAX 2550 diffractometer with Cu K α 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. 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. The TEM measurements were performed on a Hitachi H-8100 electron microscopy with an accelerating voltage of 200 kV.

1.3 Preparation of Ni₃S₂/NF, NiCO₃/NF and RuO₂/NF

Ni₃S₂/NF was prepared as follows. In a typical synthesis, a piece of NF was first treated with concentrated HCl, ethanol and deionized water by sonication sequentially to obtain a clean surface before use. To prepare Ni₃S₂ precursor using a hydrothermal reaction, NF (0.0315 g), Na₂S₂O₃ (0.24818 g) ethylenediamine (18 mL) and ethylene glycol (2 mL) were transferred to a 50 mL Teflon-lined stainless-steel autoclave in which a piece of NF was immersed into the solution. The autoclave was sealed and maintained at 180 °C for 16 h in an electric oven to obtain Ni₃S₂ precursor. After the autoclave cooled down to room temperature, the NF covered with Ni₃S₂ nanosheet array was taken out and washed with water and ethanol for several times, followed by drying at 60 °C for overnight. We prepared NiCO₃/NF via oxidative polarization of Ni₃S₂/NF for 2 h at 1.0 V vs. SCE in 1.0 M KHCO₃ (pH=8.3) at room temperature (25 °C). The loading of as-prepared NiCO₃/NF was determined to be 1.8 mg cm⁻² using a high precision microbalance. RuO₂ was prepared in accordance with reported work. Briefly, 2.61 g of RuCl₃·3H₂O and 1.0 mL KOH (1.0 mol·L⁻¹) 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. RuO₂ 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 RuO₂ ink (containing 452 μg of RuO₂) was loaded onto a bare NF of 0.25 cm⁻² in geometric area (loading: 1.8 mg·cm⁻²).

1.4 Electrochemical measurement

Electrochemical measurements were performed with a CHI 660E electrochemical analyzer (CH Instruments, Inc., Shanghai) in a standard three-electrode system. NiCO₃/NF was used as the working electrode. A graphite plate and SCE 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 (SCE) + (0.2415 + 0.059 pH) V.

1.5 TOF calculation

To compare the activity of NiCO₃/NF with other non-noble-metal catalysts, the TOF for each active site was calculated by the equation (1):

$$\text{TOF} = jA/2Fm, \quad (1)$$

where j is current density (A·cm⁻²) at defined overpotential of the electrochemical measurement in 1 mol·L⁻¹ KHCO₃; A is the geometric area of the testing electrode; 2 indicates the mole of electrons consumed for evolving one mole H₂ from water; F is the Faradic constant (96485 C·mol⁻¹); m is the number of active sites (mol), which can be extracted from the linear relationship between the oxidation peak currents and scan rates by the equation (2):

$$\text{slope} = n^2F^2A\Gamma_0/4RT, \quad (2)$$

where n is the numbers of electron transferred; Γ_0 is the surface concentration of active sites (mol·cm⁻²); R and T are the ideal gas constant and the absolute temperature, respectively.

1.6 FE determination

The FE was calculated by comparing the amount of measured H₂ generated by cathodal electrolysis with calculated H₂ (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.

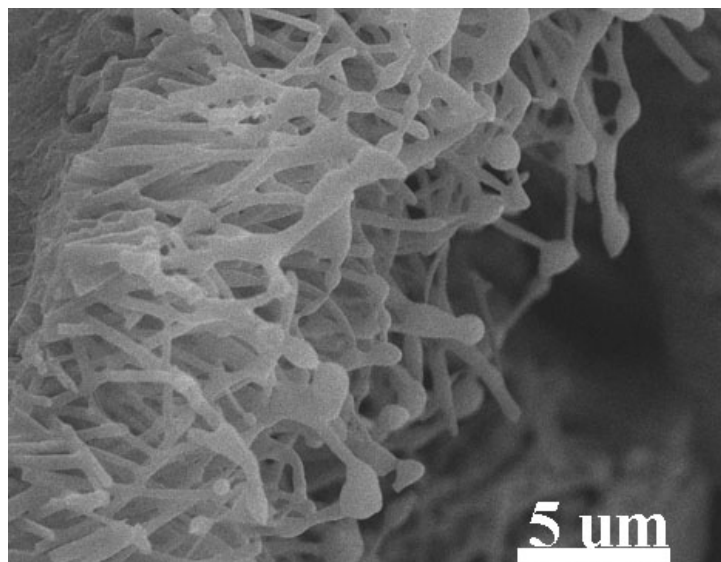


Fig. S1 Cross-section SEM image of NiCO₃/NF

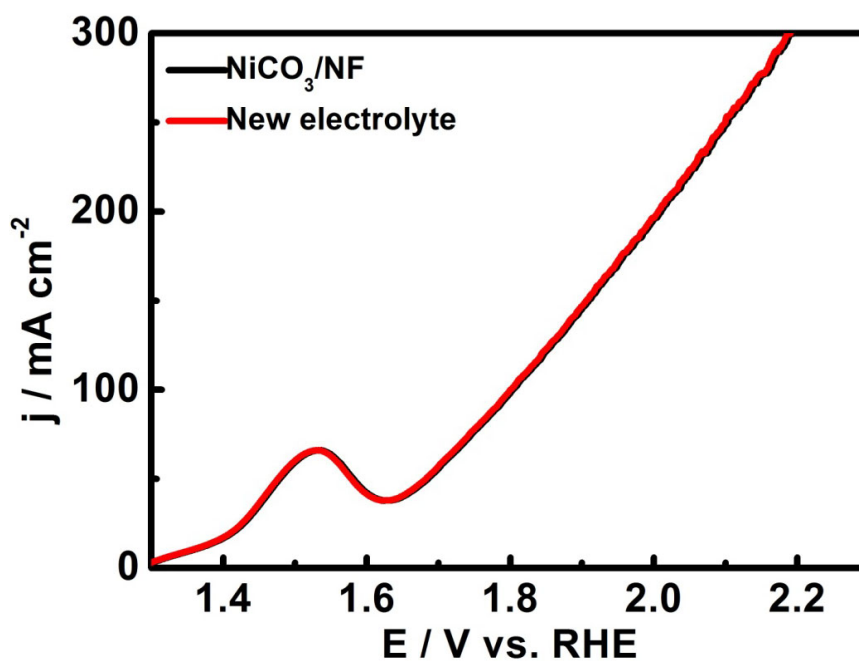


Fig. S2 LSV curves for NiCO₃/NF tested in used (black) and fresh (red) 1.0 mol·L⁻¹ KHCO₃

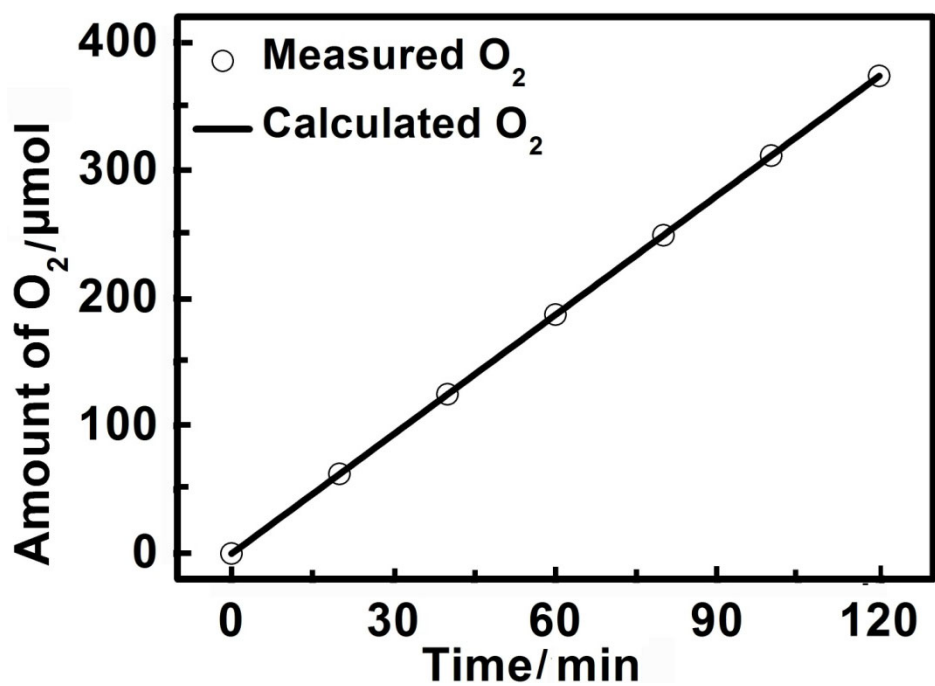


Fig. S3 Practically generated and theoretically calculated oxygen amount versus time for NiCO₃/NF in 1.0 mol·L⁻¹ KHCO₃

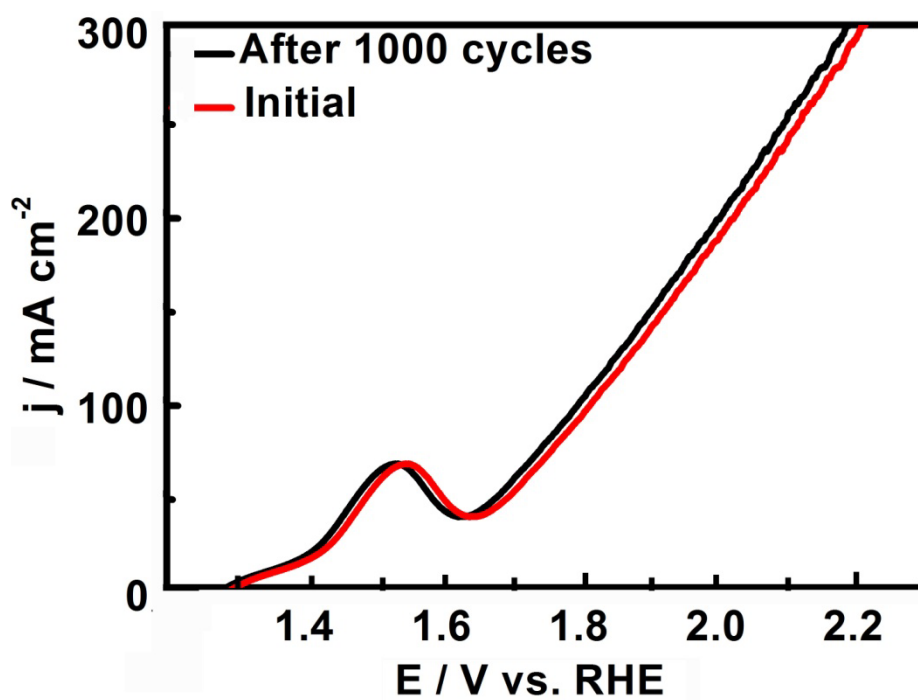


Fig. S4 LSV curves recorded for NiCO₃/NF before and after 1000 CV cycles at a scan rate of 100 mV·s⁻¹

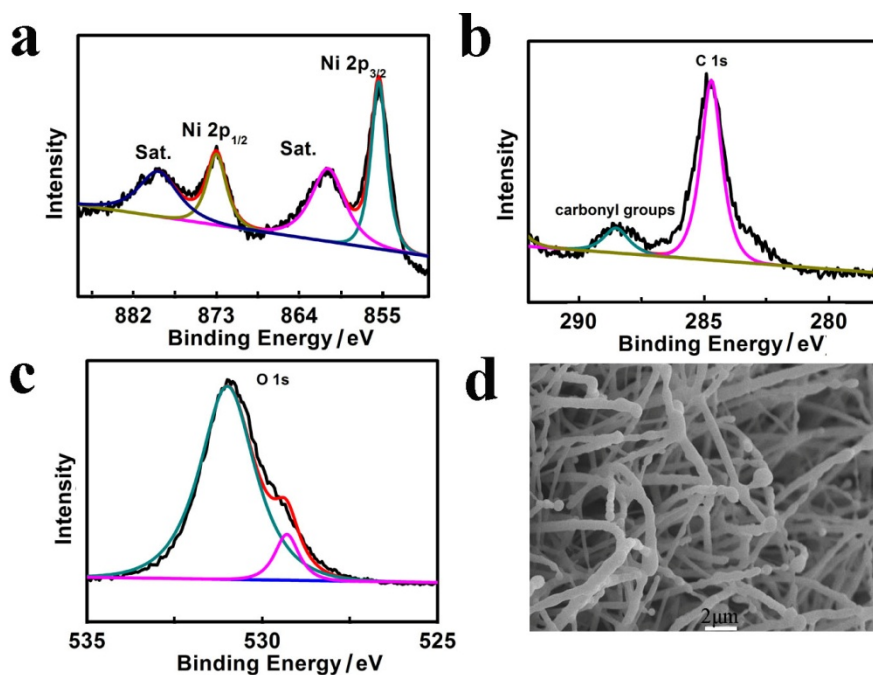


Fig. S5 XPS spectra of NiCO₃ in the (a) Ni 2p, (b) C 1s, and (c) O 1s regions for NiCO₃ after OER electrolysis. (d) SEM image for NiCO₃/NF after OER electrolysis

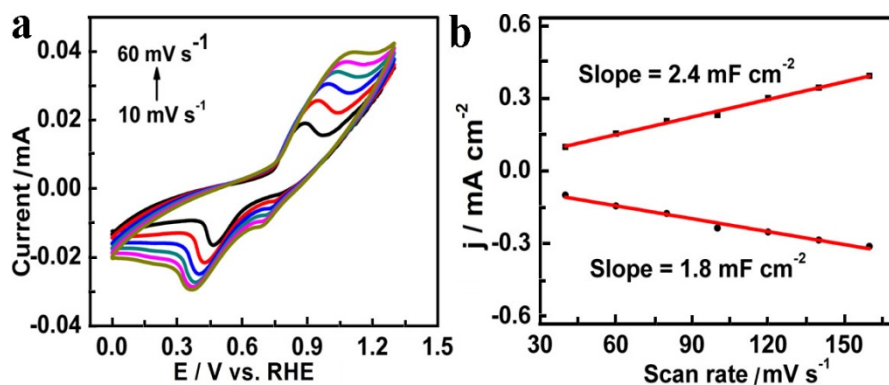


Fig. S6 (a) Cyclic voltammograms for NiCO₃ under different scan rates increasing from 0 to 60 mV·s⁻¹ in 1.0 M KHCO₃. (b) Plots of linear relationship of the oxidation peak currents vs. scan rates for NiCO₃/NF.

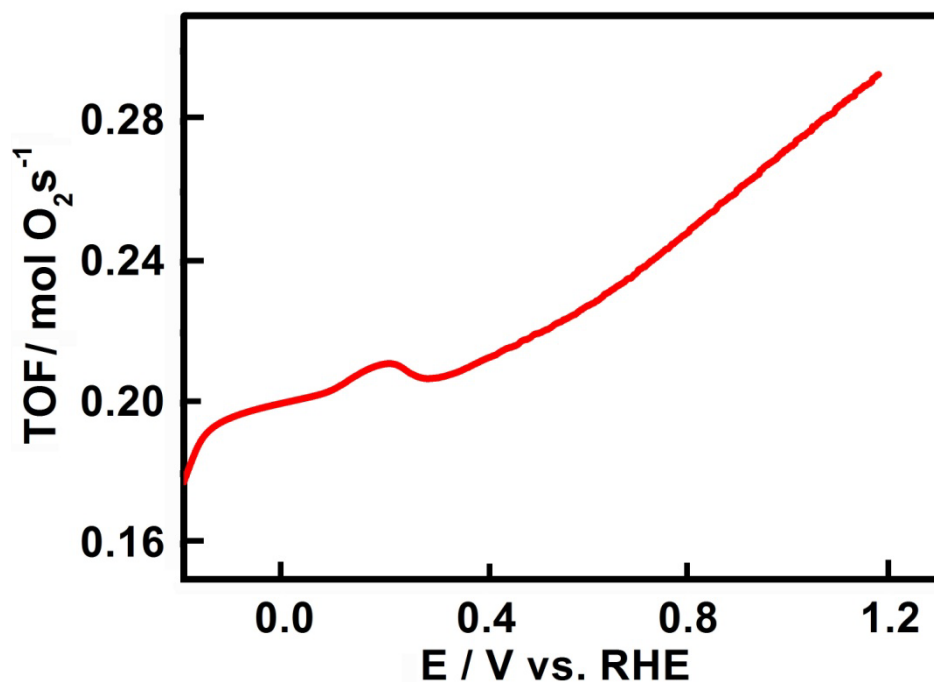


Fig. S7 Plot of TOF vs. potential for NiCO₃/NF

Table S1 Comparison of OER performance for NiCO₃/NF with other non-noble-metal electrocatalysts in neutral or near-neutral media

Catalyst	$J/$ (mA·cm ⁻²)	Loading / (mg·cm ⁻²)	TOF/ (mol O ₂ ·s ⁻¹)	η /mV	Electrolyte	Ref.
NiCO ₃ /NF	30	1.8	0.19	325	1.0 M KHCO ₃	This work
	50	1.8	0.19	395		
Fe-Ci/FTO	10	-	-	560	0.2 M Ci	[1]
Co-Ci/GC	9.1	-	-	771	0.2 M K-Ci	[2]
Ni-Bi film/ITO	1.0	-	-	425	0.1 M Bi	[3]
Ni-Bi film/FTO	1.0	-	-	390	0.5 M Bi	[4]
Co-Ni LDH/FTO	1.0	0.15	-	490	0.1 M K-Pi	[5]
Cu-Bi/FTO	1.0	-	-	525	0.2 M Na-Bi	[6]
Ni-Bi/CC	10	2.3	0.45	470	0.1 M K-Bi	[7]
Co-Pi NA/Ti	10	0.95	0.065	450	0.1 M K-Pi	[8]
Fe-Pi-Bi/CC	10	2.21	-	434	0.1 M K-Bi	[9]
FeOOH/CeO ₂	80	0.44	-	300	1.0 M NaOH	[10]
FeOOH/Co/FeOOH	50	0.5	0.284	260	1.0 M KOH	[11]

References

- [1] Li F, Chen L, Li B, Wang Y, Yu F, Sun L. An iron-based thin film as a highly efficient catalyst for electrochemical water oxidation in a carbonate electrolyte. *Chemical Communications*, 2016, 52, 5753-5756
- [2] Joya K S, Takanabe K, de Groot H J M. Surface generation of a cobalt-derived water oxidation electrocatalyst developed in a neutral HCO₃⁻/CO₂ system. *Advanced Energy Materials*, 2014, 4(16): 1400252
- [3] Dincă M, Surendranath Y, Nocera D G. Nickel–borate oxygen–evolving catalyst that functions under benign conditions. *Proceedings of the national academy of sciences of the united states of America*, 2010, 107(23): 10337–10341

- [4] Bediako D. K, Surendranath Y, Nocera D G. Mechanistic studies of the oxygen evolution reaction mediated by a nickel–borate thin film electrocatalyst. *Journal of the American Chemical Society*, 2013, 135(9): 3662–3674
- [5] Zhang Y, Cui B, Zhao C, Lin H, Li J. Co–Ni layered double hydroxides for water oxidation in neutral electrolyte. *Physical Chemistry Chemical Physics*, 2013, 15, 7363–7369
- [6] Yu F, Li F, Zhang B, Li H, Sun L. Efficient electrocatalytic water oxidation by a copper oxide thin film in borate buffer. *American Chemical Society Catalysis*, 2015, 5(2): 627–630
- [7] Ji X, Cui L, Liu D, Hao S, Liu J, Qu F, Ma Y, Du G, Asiri A. M, Sun X. A nickel–borate nanoarray: A highly active 3D oxygen–evolving catalyst electrode operating in near–neutral water. *Chemical Communications*, 2017, 53, 3070–3073
- [8] Xie L, Zhang R, Cui L, Liu D, Hao S, Ma Y, Du G, Asiri A M, Sun X. High-performance electrolytic oxygen evolution in neutral media catalyzed by a cobalt phosphate nanoarray. 2017, 129(4): 1084–1088
- [9] Wang W, Liu D, Hao S, Qu F, Ma Y, Du G, Asiri A M, Sun X. High-efficiency and durable water oxidation under mild pH conditions: An iron phosphate–borate nanosheet array as a non-noble-metal catalyst electrode. 2017, 56(6): 3131–3135
- [10] Feng J, Ye S, Xu H, Tong Y, Li G. Design and Synthesis of FeOOH/CeO₂ Heterolayered Nanotube Electrocatalysts for the Oxygen Evolution Reaction. *Advanced Materials*, 2016, 28, 4698–4703
- [11] Feng J, Xu H, Dong Y, Ye S, Tong Y, Li G. FeOOH/Co/FeOOH hybrid nanotube arrays as high-performance electrocatalysts for the oxygen evolution reaction. *Angewandte Chemie International Edition*, 2016, 55(11): 3694–3698