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Supporting information

Cobalt-borate nanowire array as a high-performance catalyst for oxygen evolution reaction at near-neutral media

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1. Materials

The NH_4F, $Co(NO_3)_2\cdot 6H_2O$, $K_2B_4O_7\cdot 5H_2O$, HCl, Se powders and urea were purchased from Beijing Chemical Corp (China). Ti mesh was purchased from Hangxu filter flagship store. The $RuCl_3\cdot 3H_2O$ and Nafion (5 wt%) were purchased from Sigma-Aldrich Chemical Reagent Co., Ltd. The ultrapure water used throughout all experiments through a Millipore system. All chemicals were used as received without further purification. The Ti mesh was pretreated with HCl solution (5 wt%) for 5 min at 373 K and wash in water/ethanol for three times to remove surface oxidation layer and impurities.

2. Experimental

Characterization: The XRD patterns were obtained from a Rigaku/MAX 2550 X-ray diffractometer with Cu Kα radiation (40 kV, 30 mA) of wavelength 0.154 nm (RIGAKU, Japan). Scanning electron microscopy (SEM) were collected from the tungsten lamp-equipped SU3500 scanning electron microscope at an accelerating voltage of 20 kV (HITACHI, Japan). Transmission electron microscopy (TEM) images were obtained from a Zeiss Libra 200FE transmission electron microscope operated at 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source.

Preparation of Co(OH)F NA/Ti: 1 mmol $Co(NO_3)_2\cdot 6H_2O$, 2 mmol NH_4F, and 5 mmol urea were dissolved in 25 mL ultrapure water under magnetic stirring to form a uniform pink solution. Then, the pre-treated Ti mesh (Details in SI) and the above pink solution were transferred into a 50 mL Teflon-lined stainless-steel autoclave and maintained at 378 K for 5 h. After cooled to room temperature, the product was washed with ultrapure water for several times. Then the Co(OH)F NA/Ti was obtained.

Preparation of $CoSe_2$ NA/Ti: The $CoSe_2$ NA/Ti was obtained by chemical vapor deposition (CVD) method. Detailed, 0.5 g Se powders and a piece of Co(OH)F NA/Ti were put in two individual porcelain boat. The Se powders were heated to 573 K in upstream with a heating speed of 1.5 K min^{-1} under Ar flow. The Co(OH)F NA/Ti was heated to 673 K in downstream with a heating speed of 2 K min^{-1} under Ar flow. The two individual heating zones were kept at each temperature for 120 min. The furnace was then allowed to cool to room temperature in Ar atmosphere. The pictures of the bare Ti mesh, Co(OH)F NA/Ti, $CoSe_2$ NA/Ti are shown in Fig. S7, indicating the successfully synthesis.

Preparation of Co-Bi NA/Ti: In this experiment, the Co-Bi was formed with a rapid electrochemical topotactic conversion. The prepared $CoSe_2$ NA/Ti was conducted in a typical three-electrode equipment (saturated calomel electrode as the reference electrode; graphite as the counter electrode). The potential was set as 1 V, and the $CoSe_2$ NA/Ti can be transformed to Co-Bi NA/Ti in a few seconds. The detailed description synthesis process is displayed in Scheme 1.

Preparation of RuO_2 and RuO_2/Ti: The RuO_2 was prepared according to a previous report.[1] Briefly, 1.0 mL NaOH (1.0 M) and 2.61 g $RuCl_3 \cdot 3H_2O$ were added into 100 mL ultrapure water and ultrasound for 30 min at 373 K. The precipitates were collected by centrifugation and washed with water for three times. The obtained solids were dried at 353 K. Finally, the product was annealed at 573 K for 3 h under air atmosphere. The RuO_2 ink was prepared by dispersing 20 mg of RuO_2 catalyst into 490 μL of water/ethanol (v/v = 1:1) solvent containing 10 μL of 5 wt% Nafion and sonicated for 1 h. Then 15 μL of the RuO_2 ink was loaded onto a bare Ti mesh of 0.25 cm^{-2} in geometric area. The RuO_2/Ti was prepared well.

Electrochemical measurement: The electrochemical measurements were performed on a CHI 660E electrochemical workstation (Chenhua, Shanghai). A three-electrode system was used in the experiment: a graphite plate was used as the counter electrode; a saturated calomel electrode (SCE) was used as the reference electrode and the as-prepared Co-Bi NA/Ti was used as the working electrode. All the measurements were performed at 298 K in 0.1 M K-Bi except special illustration. The reference electrode was calibrated to the reversible hydrogen electrode (RHE): E (RHE) = E (SCE) + (0.242 + 0.059 pH) V.

Turnover frequency (TOF) calculation: To compare the activity of Co-Bi with other non-noble-metal catalysts, the TOF for each active site was calculated by the equation (1):[2]

$$\mathrm{TOF} = \mathrm{JA}/4\mathrm{Fm} \qquad (1)$$

Where J is current density (A cm^{-2}) at defined overpotential of the electrochemical measurement in 0.1 M K-Bi; A is the geometric area of the testing electrode; 4 indicates the mole of electrons consumed for evolving one mole O_2; 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):[3]

$$\mathrm{slope} = n^2F^2A\Gamma_0/4RT \qquad (2)$$

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.

FE determination: The FE was calculated by comparing the amount of measured O_2 generated by potentiostatic anodic electrolysis with calculated O_2 (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.

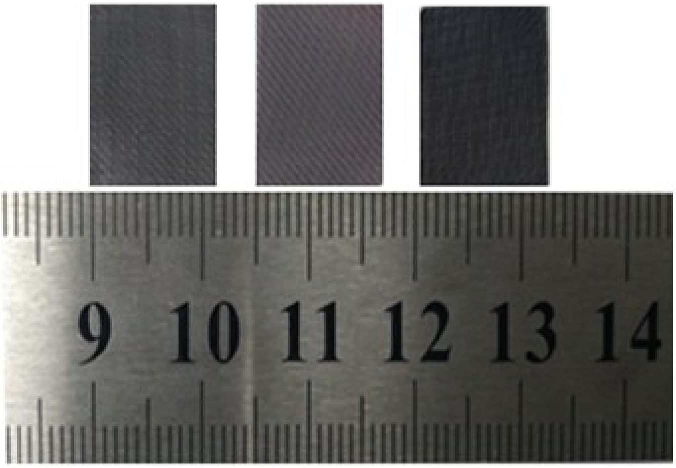

Fig. S1 Photograph of Ti mesh (left), Co(OH)F NA/Ti (middle) and $CoSe_2$ NA/Ti (right).

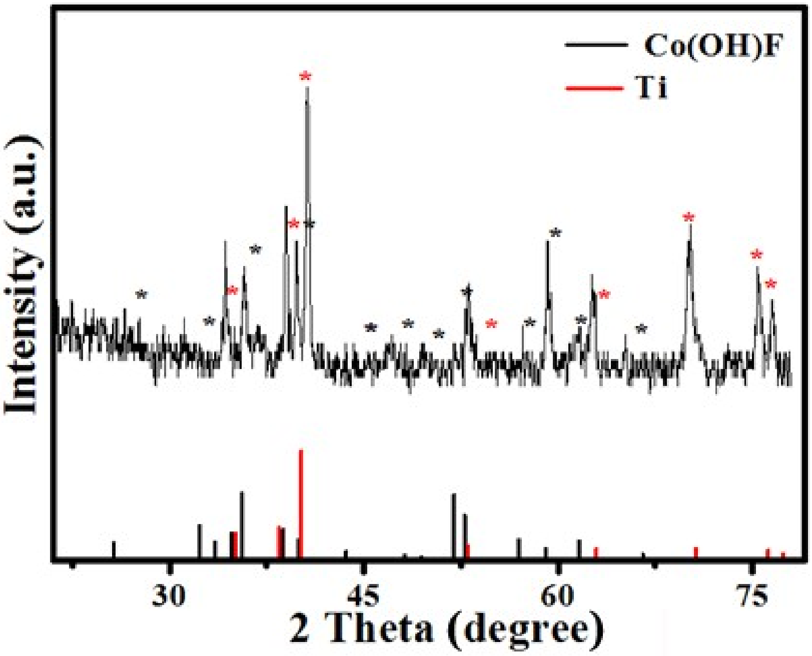

Fig. S2 XRD pattern of Co(OH)F NA/Ti.

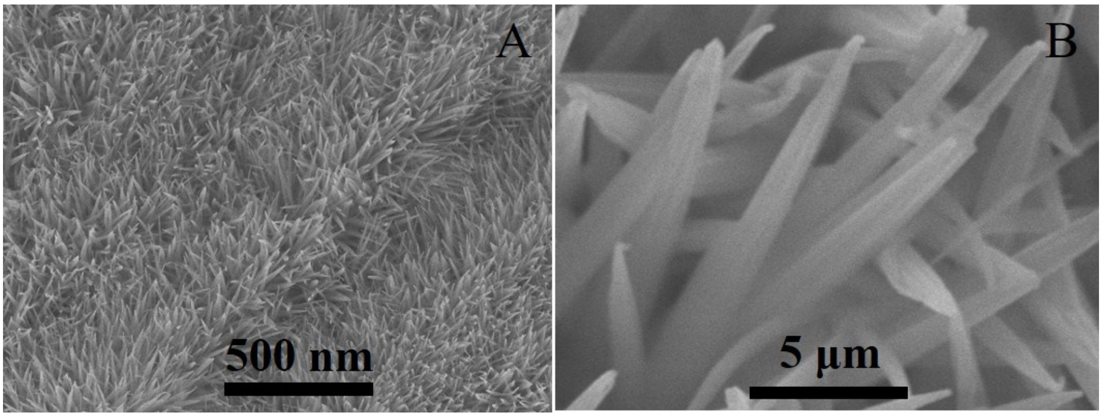

Fig. S3 SEM images (A) low- and (B) high- amplification of Co(OH)F NA/Ti.

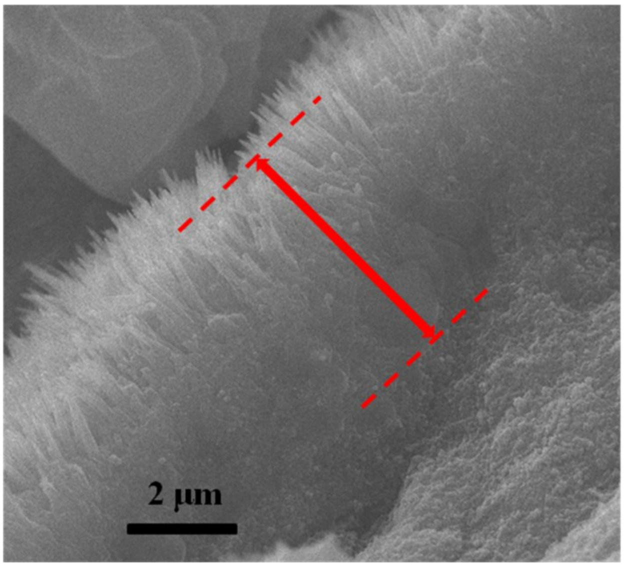

Fig. S4 The lateral image of $CoSe_2$ NA/Ti.

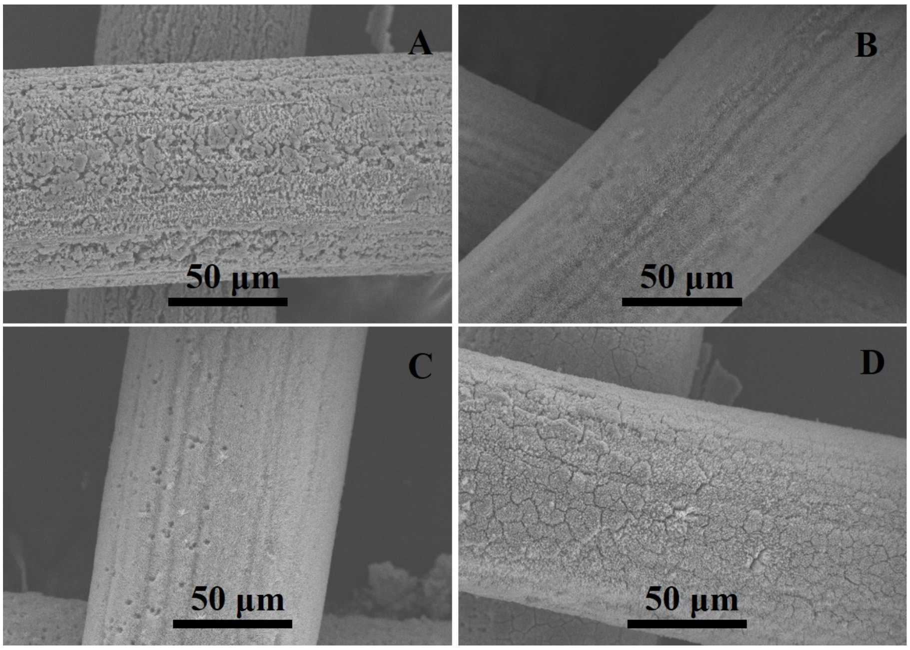

Fig. S5 Low-magnification SEM images of (A) Ti mesh, (B) Co(OH)F NA/Ti, (C) $CoSe_2$ NA/Ti, (D) Co-Bi NA/Ti.

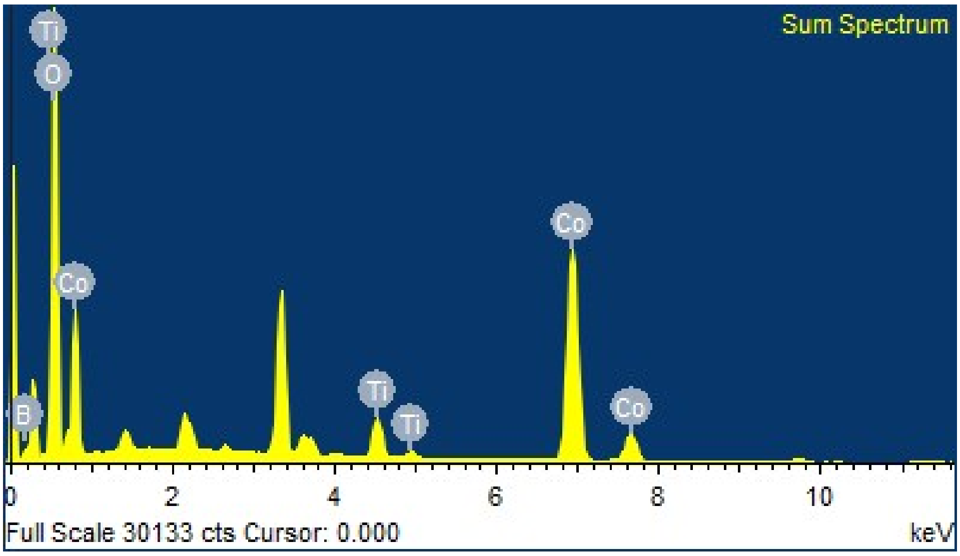

Fig. S6 EDX analysis of as-synthesized Co-Bi NA/Ti.

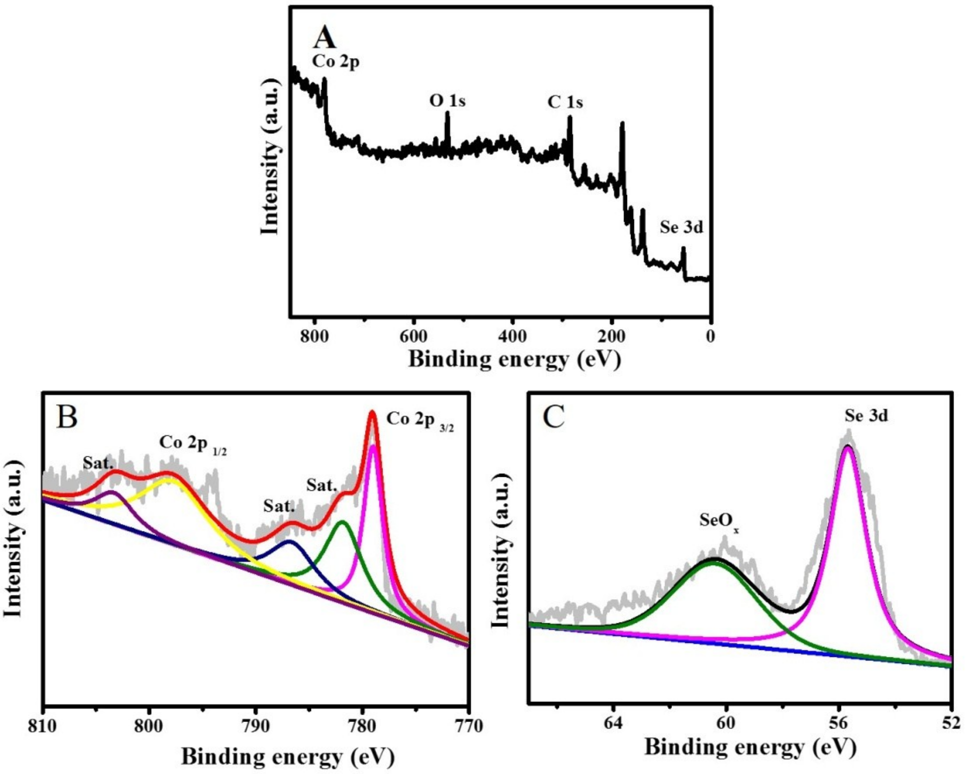

Fig. S7 XPS survey spectrum for (A) $CoSe_2$ NA. XPS spectra of $CoSe_2$ NA in the (B) Co 2p, (C) Se 3d.

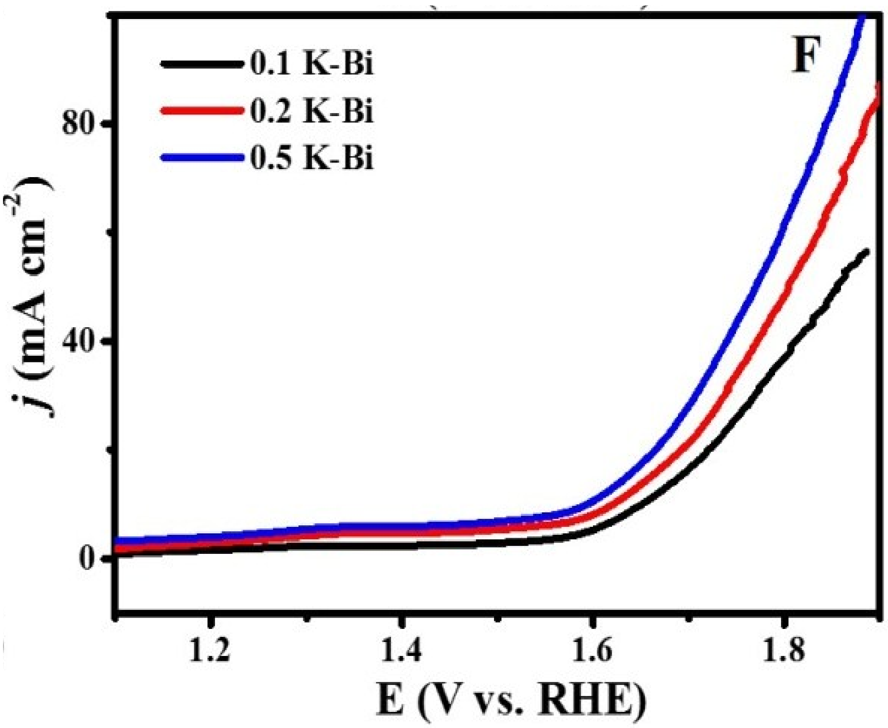

Fig. S8 LSV curves for Co-Bi NA/Ti in 0.1, 0.2, and 0.5 M K-Bi with a scan rate of 5 mV s^{-1} for OER.

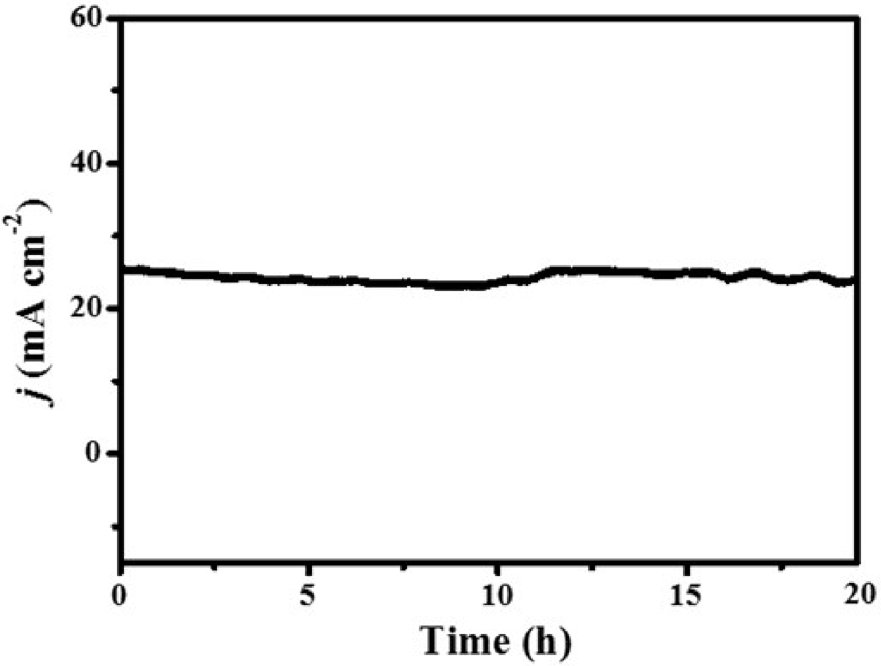

Fig. S9 Time-dependent current density curve for Co-Bi NA /Ti in 0.5 M K-Bi.

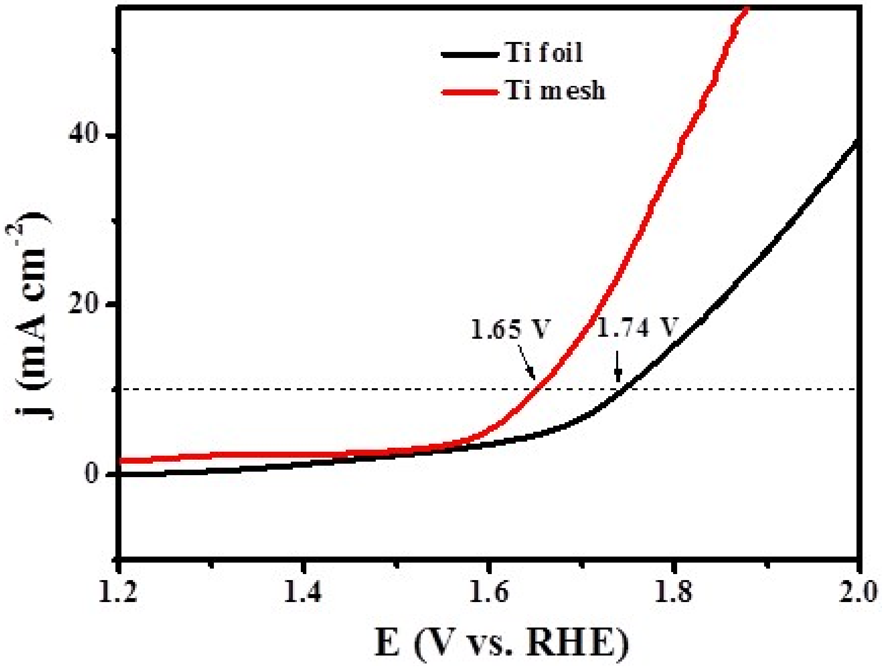

Fig. S10 LSV curves for Co-Bi NA/Ti, and Co-Bi NA on Ti foil with a scan rate of 5 mV s^{-1} for OER in 0.1 M K-Bi.

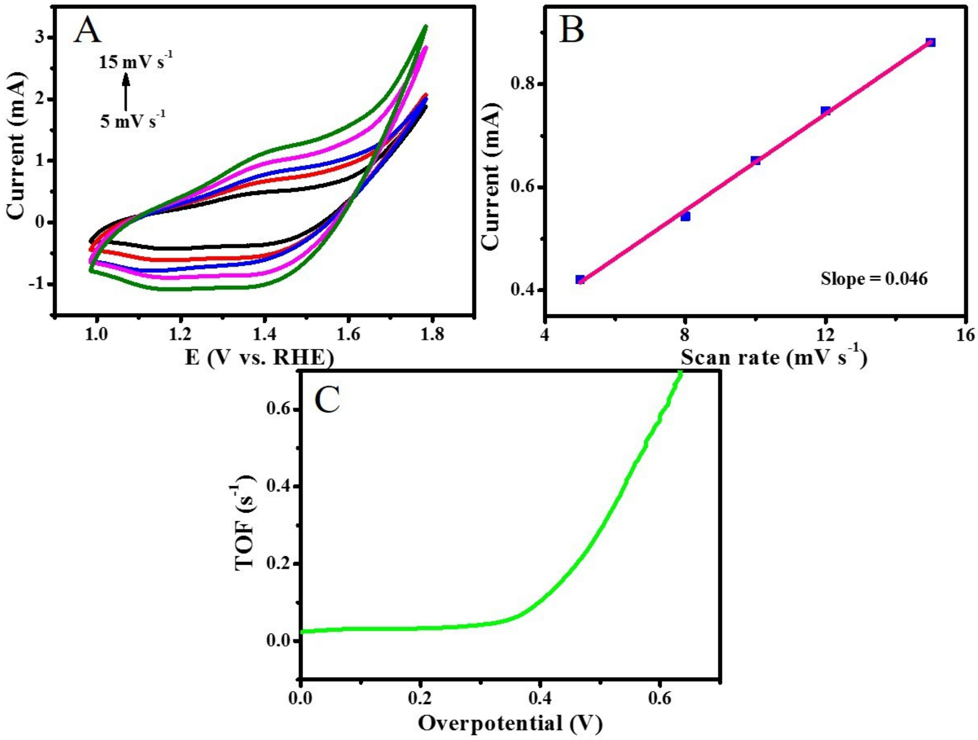

Fig. S11 (A) CVs of Co-Bi NA/Ti at different scan rates in 0.1 M K-Bi. (B) Oxidation peak current versus scan rate plot for Co-Bi NA/Ti. (C) The relationship between TOFs and overpotentials.

Table S1. Comparison of OER performance for Co-Bi NA/Ti with other non-noble-metal electrocatalysts in benign media.

Catalyst	j (mA cm^{-2})	η (mV)	Electrolyte	References
Co-Bi NA/Ti	5	363	0.1 M K-Bi	This work
	10	420		
Co-Bi NS/G	1	235	0.1 M PBS	[4]
	10	~ 490		
Co-Pi/ITO	1	410	0.1 M PBS	[5]
Co-Pi/ITO	1	483	0.1 M PBS	[6]
Co-OEC/Ni foam	100	442	1.0 M PBS	[7]
$Co(PO_3)_2$	10	590	0.1 M PBS	[8]
Cu-doped CCO	1	653	0.1 M PBS	[9]
Co-W	1	420	0.05 M PBS	[10]
$Co(OH)_2$	1	710	0.1 M PBS	[11]
CoHCF	1	580	0.05 M PBS	[12]
Co-Bi/FTO	1	390	1 M K-Bi	[13]
Fe-Bi film	1	490	0.5 M BBS	[14]
Cu-Bi/FTO	10	810	0.2 M BBS	[15]
Ni-Bi film/FTO	1	540	0.5M K-Bi	[16]
NiO_x-Bi	1	650	0.5M K-Bi	[17]
NiO_x-Fe-Bi	5	552	0.5M K-Bi	[17]
Fe-Ci/FTO	10	560	0.2 M Na-Ci	[18]
Co-Pi NA/Ti	10	450	0.1 M K-Pi	[19]

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