

## Electronic Supplementary Information

### Experimental section

**Materials:** Ti mesh was purchased from Hangxu filter flagship store.  $\text{HNO}_3$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NH}_4\text{F}$  and urea were purchased from Beijing Chemical Works. Nafion (5 wt%) and  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  were bought from Sigma-Aldrich Chemical Reagent Co., Ltd.  $\text{K}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$  was provided by Chengdu Kelon Chemical Reagent Factory. The water used throughout all experiments was purified through a Millipore system. All the reagents and chemicals were used as received without further purification.

**Synthesis of Co(OH)F/TM:** Co(OH)F/TM precursor was prepared as follows.  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.582 g), urea (0.61 g), and  $\text{NH}_4\text{F}$  (0.186 g) were dissolved in 40 mL distilled water. After gentle stirring for 20 min, the clear solution was transferred to a 50 mL Teflon-lined stainless steel autoclave and then a piece of Ti mesh (2 cm  $\times$  4 cm) 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 at room temperature, the resulting Co(OH)F/TM was taken out and washed with distilled water and ethanol several times, followed by drying at 60 °C for 2 h.

**Synthesis of CoB<sub>2</sub>O<sub>4</sub>/TM and Co-Bi/TM:** CoB<sub>2</sub>O<sub>4</sub>/TM was prepared by hydrothermal reaction. In a typical synthesis,  $\text{K}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$  (0.122 g) was dissolved in 40 mL water under vigorous stirring for 15 min. Then the solution was transferred into a Teflon-lined stainless autoclave (50 mL) and the as-prepared Co(OH)F/TM was immersed into the solution. The autoclave was sealed and maintained at 110 °C for 5 h in an electric oven. After cooled down naturally to room temperature, the CoB<sub>2</sub>O<sub>4</sub>/TM was taken out and washed with distilled water and ethanol several times, followed by drying at 60 °C for 2 h. To obtain Co-Bi/TM, Co(OH)F/TM as the working electrode performed in 0.1 M K-Bi (pH = 9.2) until the current density levelled off, with a platinum wire as the counter electrode and Ag/AgCl as the reference electrode.

**Synthesis of RuO<sub>2</sub>:** RuO<sub>2</sub> was prepared according to previous publication.<sup>1</sup> Briefly, 2.61 g of  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  and 30 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 and washed with water several times. Finally, the product was dried at 80 °C overnight and then annealed at 350 °C in air atmosphere for 1 h.

**Characterizations:** X-ray diffraction (XRD) measurements were operated using a RigakuD/MAX 2550 diffractometer with Cu K $\alpha$  radiation ( $\lambda=1.5418$  Å). Scanning electron microscope (SEM) measurements were conducted on a XL30 ESEM FEG scanning electron microscope with an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) images were recorded on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) at an accelerating voltage of 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 setup using a CoB<sub>2</sub>O<sub>4</sub>/TM as the working electrode. A platinum wire 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%. All potentials reported in this work were calibrated to RHE unless especially illustrated, using the following equation:  $E(\text{RHE}) = E(\text{Ag/AgCl}) + (0.197 + 0.059 \text{ pH}) \text{ V}$ .

**Turnover frequency (TOF) calculations:** For TOF calculations, the surface concentration of active sites associated with the redox Co species should be first calculated, and the linear relationship between the oxidation peak current and scan rate is extracted from the electrochemical cyclic voltammetry scans. The slope of the line can be calculated based on the following equation:

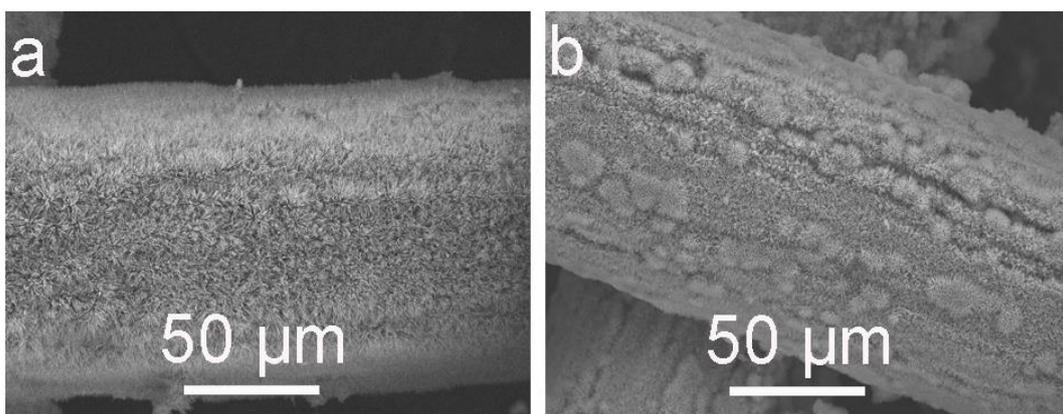
$$\text{Slope} = n^2 F^2 A \Gamma_0 / 4RT$$

Where  $n$  is the number of electrons transferred;  $F$  is Faraday's constant;  $A$  is the surface area of the electrode;  $\Gamma_0$  is the surface concentration of active sites ( $\text{mol cm}^{-2}$ ), and  $R$  and  $T$  are the ideal gas constant and the absolute temperature, respectively.<sup>2</sup>

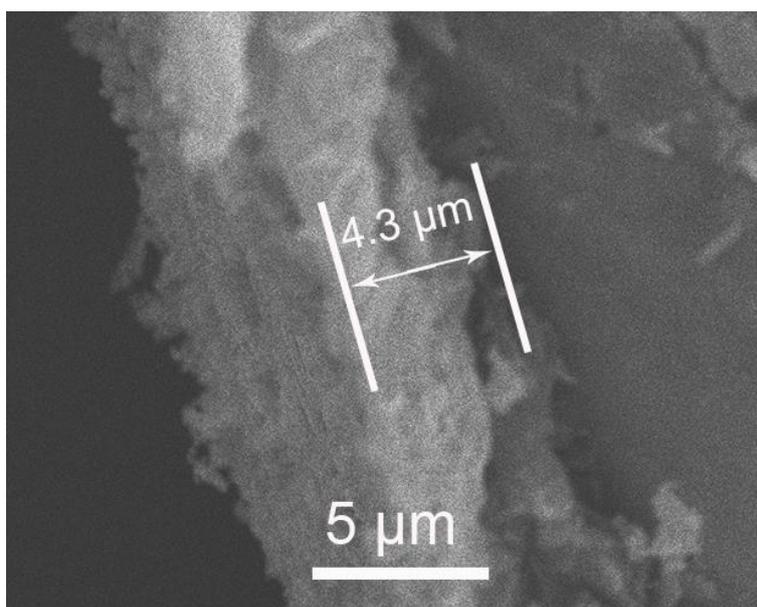
TOF values can be finally calculated from the formula:

$$\text{TOF} = JA/4Fm$$

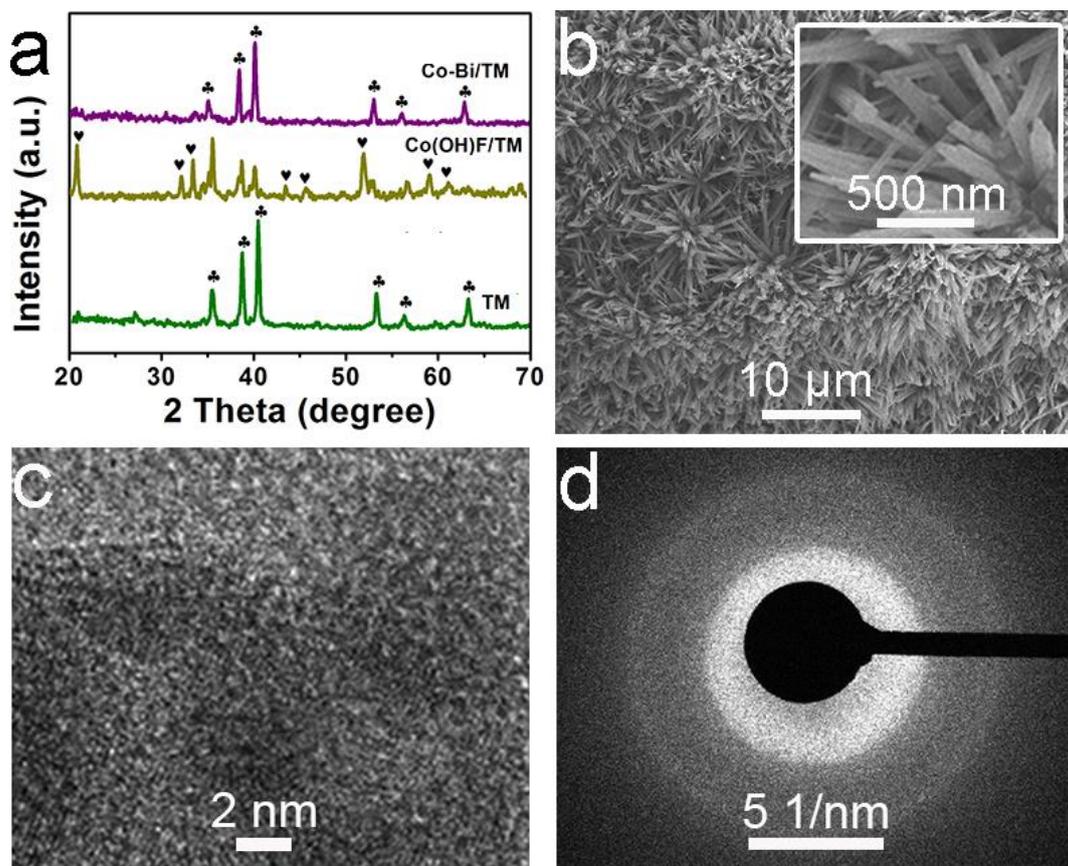
Where J is the current density at a certain overpotential, A is the area of the electrode, 4 indicates the mole of electrons consumed for evolving one mole of O<sub>2</sub> from water, F is Faraday's constant and m is the number of moles of active sites.<sup>3</sup>



**Fig. S1.** SEM images of (a) Co(OH)F/TM and (b) CoB<sub>2</sub>O<sub>4</sub>/TM.



**Fig. S2.** Cross-section SEM image of CoB<sub>2</sub>O<sub>4</sub>/TM.



**Fig. S3.** (a) XRD pattern for Co-Bi/TM, Co(OH)F/TM, and bare TM. (b) SEM images for Co-Bi/TM. (c) HRTEM image (d) selected area electron diffraction pattern taken from Co-Bi nanowire.

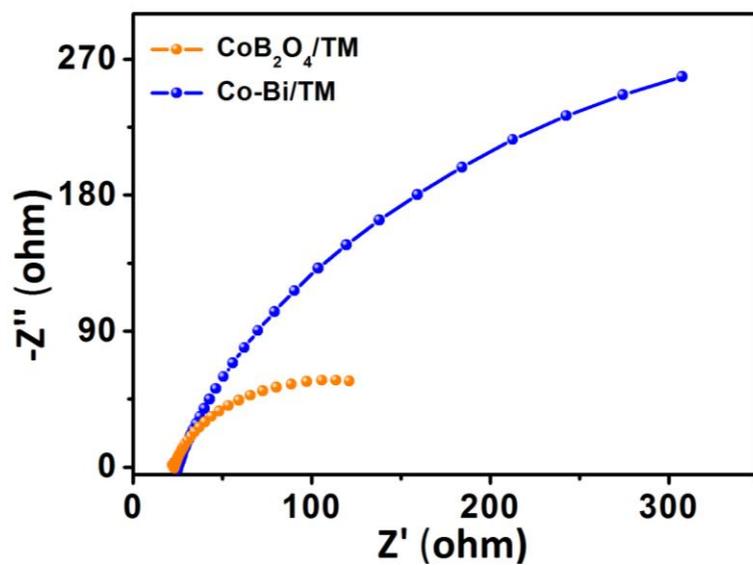
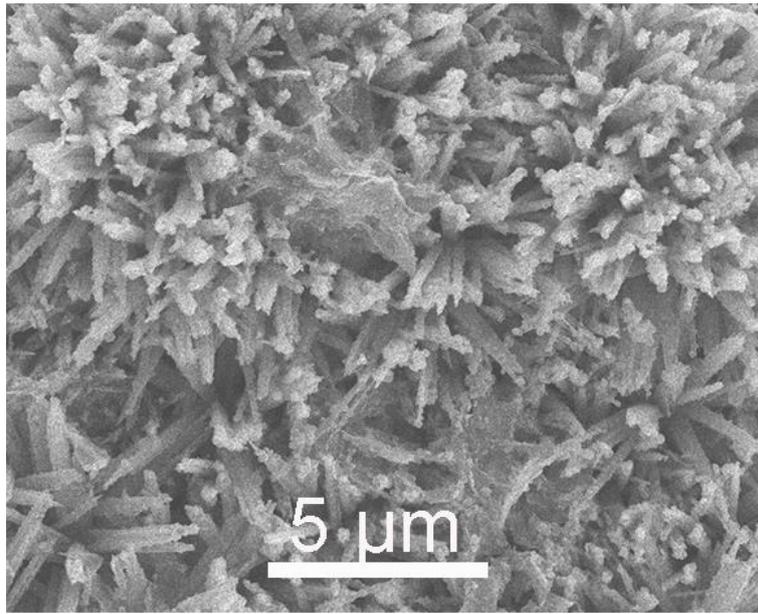
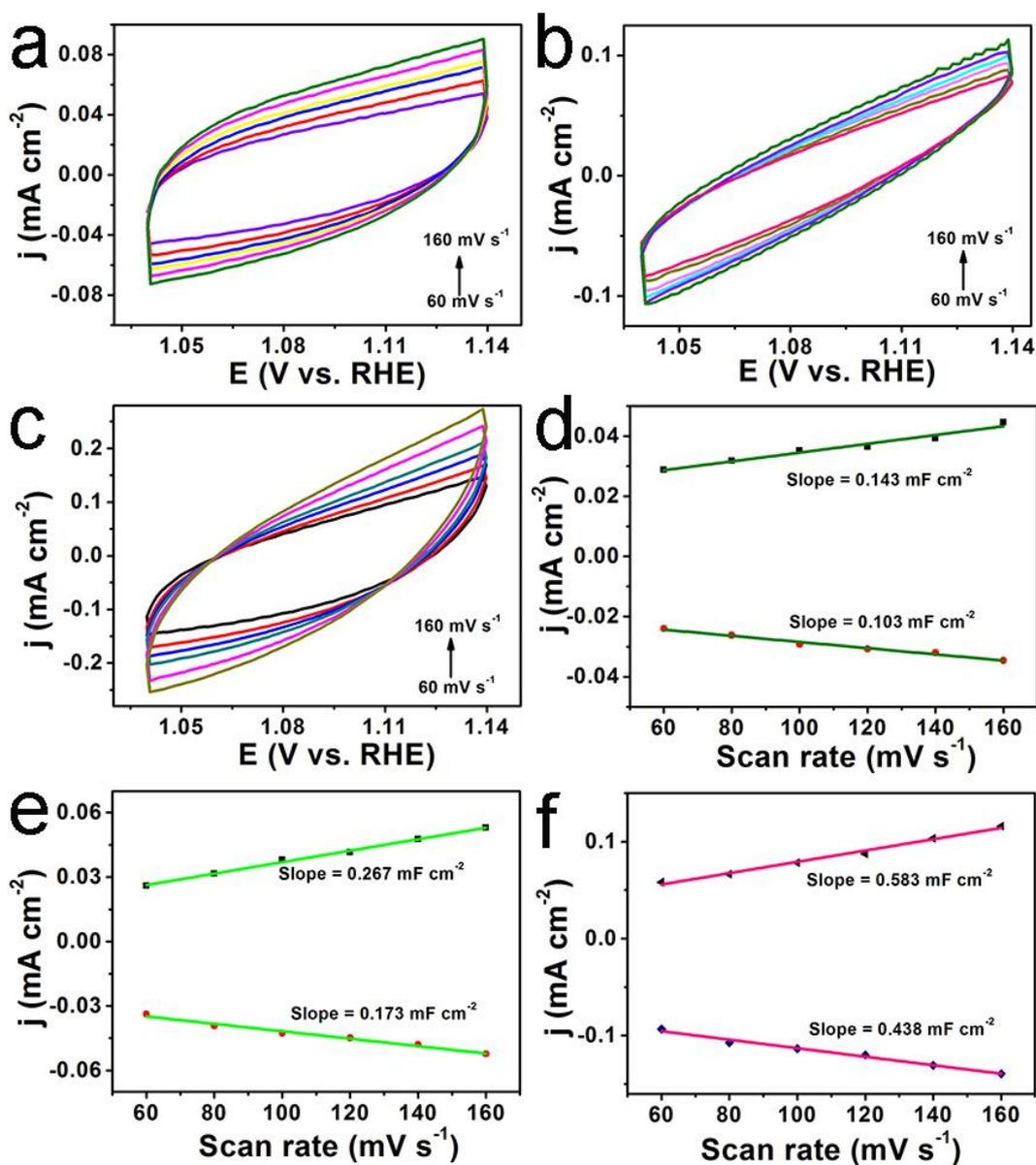


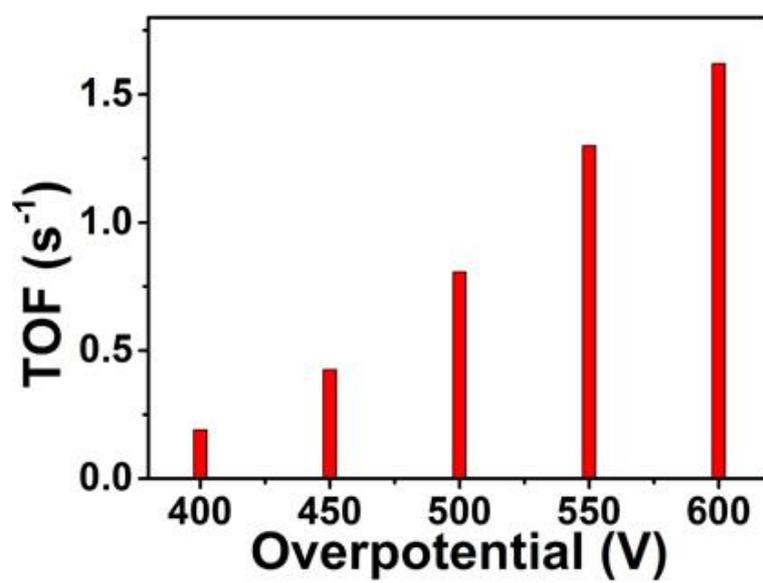
Fig. S4. Nyquist plots for Co-Bi/TM and CoB<sub>2</sub>O<sub>4</sub>/TM recorded in 0.1 M K-Bi.



**Fig. S5.** SEM image for  $\text{CoB}_2\text{O}_4/\text{TM}$  after 1000 cycles in 0.1 M K-Bi.



**Fig. S6.** CVs for (a) Co(OH)F/TM, (b) Co-Bi/TM, and (c) CoB<sub>2</sub>O<sub>4</sub>/TM in the non-faradaic capacitance current range at scan rates of 60, 80, 100, 120, 140, and 160 mV s<sup>-1</sup> in 0.1 M K-Bi. Corresponding capacitive currents at 1.09 V as a function of scan rate for (d) Co(OH)F/TM, (e) Co-Bi/TM, and (f) CoB<sub>2</sub>O<sub>4</sub>/TM.



**Fig. S7.** TOF values for  $CoB_2O_4/TM$  at different fixed overpotentials.

**Table S1.** Comparison of water oxidation performance for CoB<sub>2</sub>O<sub>4</sub>/TM with other non-noble-metal electrocatalysts under mild conditions.

Catalyst	$j$ (mA cm <sup>-2</sup> )	$\eta$ (mV)	Electrolyte	Ref.
CoB <sub>2</sub> O <sub>4</sub> /TM	2	354	0.1 M K-Bi	This work
	5	403		
	10	446		
Co-Bi film/GC	1	395	0.1 M K-Bi	4
Co-Bi NS/G	14.4	570	0.1 M PBS	5
Co <sub>3</sub> O <sub>4</sub> nanorods	4.7×10 <sup>-6</sup>	385	0.1 M PBS	6
Co-W film/FTO	1	420	0.05 M Na <sub>2</sub> WO <sub>4</sub>	7
Co-Mo film/FTO		500	0.06 M Na <sub>2</sub> MoO <sub>4</sub>	
CoO/CoSe <sub>2</sub> -Ti	10	510	0.5 M PBS	8
CCH@Co-Pi NA/Ti	10	460	0.1 M PBS	9
Au-Co(OH) <sub>2</sub>	1	410	0.1 M PBS	10
Fe-based film/ITO	1	480	0.1 M PBS	11
A-Fe film/ITO	10	600	0.5 M BBS	12
Fe-Ci film/FTO	10	560	0.2 M CBS	13
NiO <sub>x</sub> -Bi film	1	650	0.5 M K-Bi	14
NiFeO <sub>x</sub> -Bi film	5	552		
NiO <sub>x</sub> -Cat film/GC	1.15	605	0.2 M CBS	15
NiO <sub>x</sub> -en film/FTO	1.8	610	0.6 M Na-Bi	16
O <sub>2</sub> -NiO <sub>x</sub> /MWCNT film	0.5	330	0.1 M K-Bi	17
Ni-Bi film/ITO	1	425	0.1 M BBS	18
O <sub>2</sub> -NiCat/FTO	0.6	618	0.1 M Na-Bi	19
NiFe-LDH@NiFe-Bi/CC	5	415	0.1 M K-Bi	20
Partially oxidized MnO NCs	5	530	0.3 M PBS	21

CuO/FTO	0.1	430	0.1 M K-Bi	22
O <sub>2</sub> -CuCat/FTO	0.18	320	0.1 M K-Bi	23

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