Electronic Supplementary Information

Experimental section

Materials: Carbon cloth (CC) was provided by Hongshan District, Wuhan Instrument Surgical Instruments business. HNO_3, $Co(NO_3)_2·6H_2O$, NH_4F and urea were purchased from Beijing Chemical Works. $Fe(NO_3)_3·9H_2O$ was purchased from Tianjin Fuyu Chemical Reagent Co. Ltd. (China). Nafion (5 wt%) and $RuCl_3·3H_2O$ were purchased from Sigma-Aldrich Chemical Reagent Co., Ltd. $K_2B_4O_7·4H_2O$ 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.

Preparation of Fe-Co_3O_4/CC and Co_3O_4/CC: FeCo-hydroxide nanoarray was prepared as follows. $Co(NO_3)_2·6H_2O$ (2 mmol), $Fe(NO_3)_3·9H_2O$ (1 mmol), urea (15 mmol) and NH_4F (8 mmol) were dissolved in 50 mL distilled water. After gentle stirring for 15 min, the clear solution was transferred to a 50 mL Teflon-lined stainless steel autoclave and a piece of CC (2 cm × 4 cm) because its flexible feature is preferred for practical uses in technological devices.[1] And CC was cleaned by sonication in water and ethanol for 10 min, 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 FeCo precursor was taken out and washed with water and ethanol several times, followed by drying at 60 °C. Subsequently, the sample was annealed at 400 °C in air for 2 h to obtain the Fe-Co_3O_4/CC. Co_3O_4/CC was made without the addition of $Fe(NO_3)_3·6H_2O$.

Synthesis of Fe-Co_3O_4@Fe-Co-Bi/CC and Co_3O_4-derived nanoarray catalyst: To obtain Fe-Co_3O_4@Fe-Co-Bi/CC, Fe-Co_3O_4/CC was treated at 1.1 V (vs. Ag/AgCl) in 0.1 M K-Bi (pH 9.2) for 0.5 h. Co_3O_4-derived nanoarray catalyst was similarly prepared from Co_3O_4/CC.

Synthesis of RuO_2: RuO_2 was prepared according to previous publication.[2] Briefly, 2.61 g of $RuCl_3·3H_2O$ 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 and washed with water several times. Finally, the product was dried at 80 °C overnight and then annealed at 300 °C in air atmosphere for 3 h.

Characterizations: Powder X-ray diffraction (XRD) patterns were performed using a RigakuD/MAX 2550 diffractometer with Cu Kα radiation (λ=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 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. Fe-Co_3O_4@Fe-Co-Bi/CC was used 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%. 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.

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 CV scans. The slope of the line can be calculated based on the following equation:

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

Where n is the number of electrons transferred; F is Faraday's constant; A is the surface area of the electrode; Γ_0 is the surface concentration of active sites (mol cm^{-2}), and R and T are the ideal gas constant and the absolute temperature, respectively.[3]

TOF values can be finally calculated from the formula:

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

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_2 from water, F is Faraday's constant and m is the number of moles of active sites.[4]

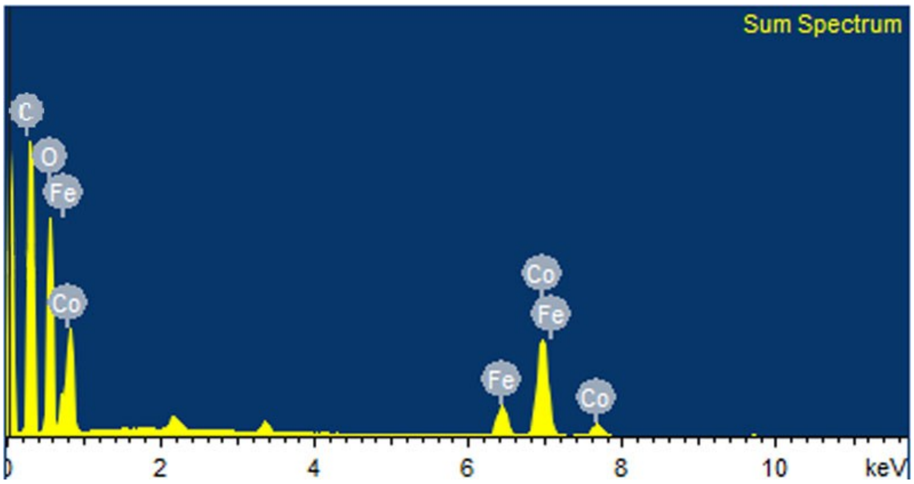

Fig. S1. EDX spectrum for Fe-Co_3O_4/CC.

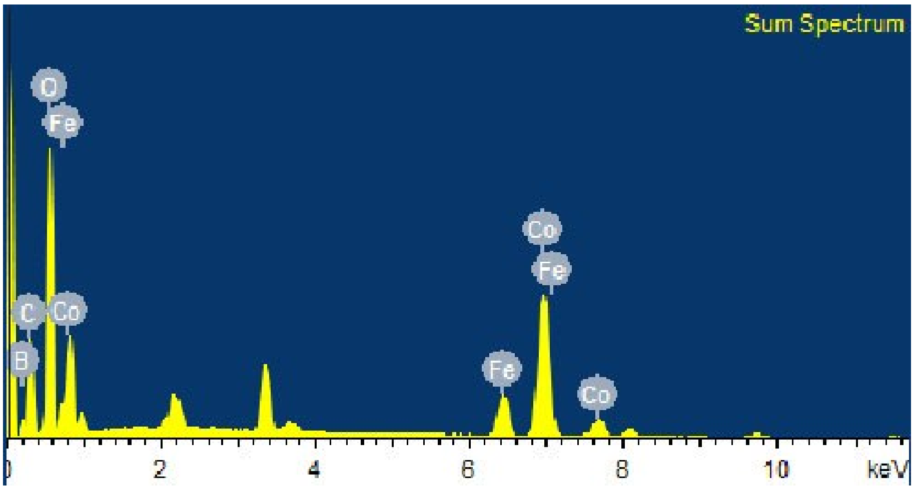

Fig. S2. EDX spectrum for Fe-Co_3O_4@Fe-Co-Bi/CC.

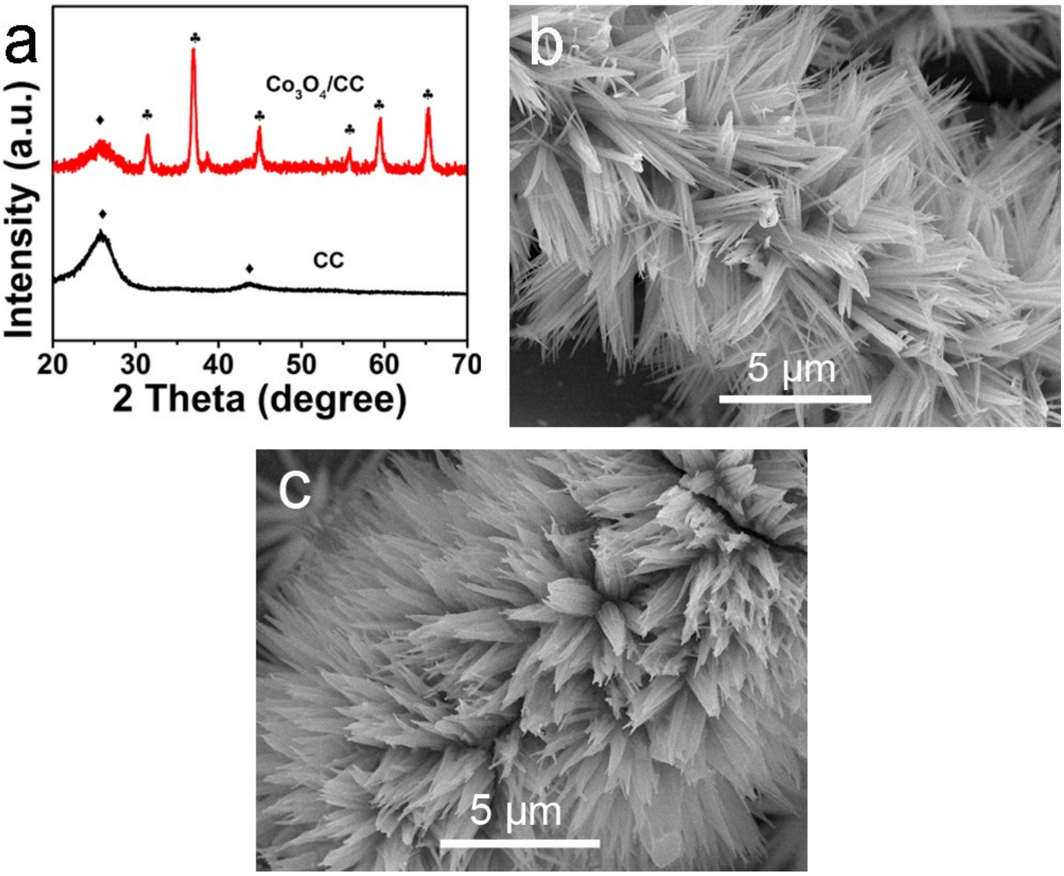

Fig. S3. (a) XRD patterns of bare CC and Co_3O_4/CC. SEM images for (b) Co_3O_4/CC and (c) Co_3O_4-derived nanoarray catalyst.

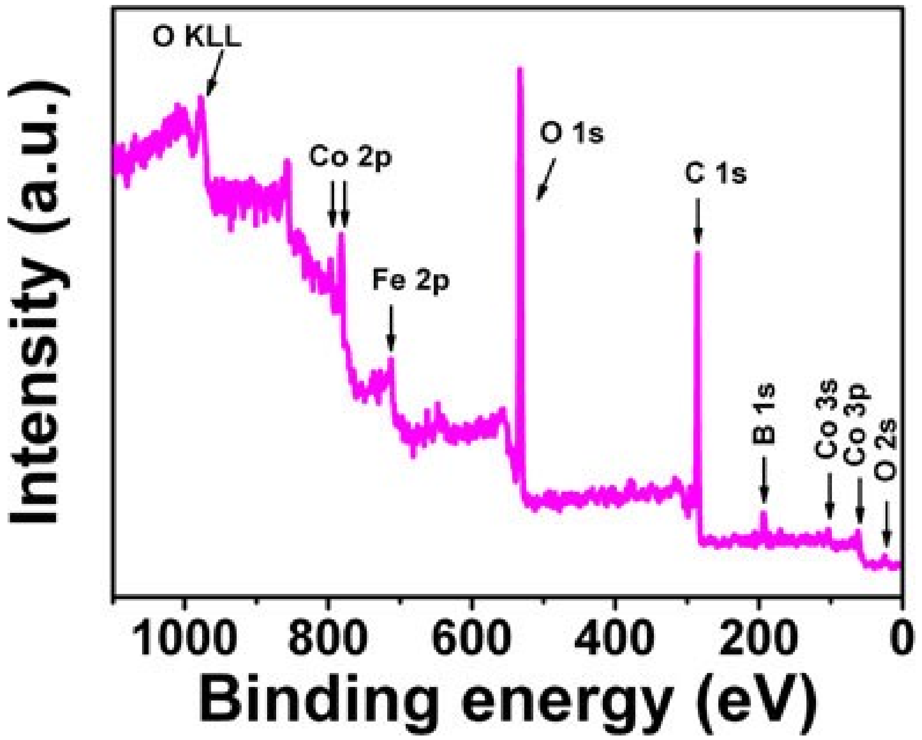

Fig. S4. XPS survey spectrum for Fe-Co_3O_4@Fe-Co-Bi.

Table S1. Comparison of OER performance for Fe-Co_3O_4@Fe-Co-Bi/CC with other non-noble-metal electrocatalysts in benign media.

Catalyst	j (mA cm^{-2})	η (mV)	Electrolyte	Ref.
Fe-Co_3O_4@Fe-Co-Bi/CC	5	383	0.1 M K-Bi	This work
	10	420		
	20	480		
	20	470	0.3 M K-Bi	
	20	460	0.5 M K-Bi	
Co-Bi film/GC	1	395	0.1 M K-Bi	5
Co-Pi NA/Ti	10	450	0.1 M PBS	6
Co-Pi/ITO	1	410	0.1 M PBS	7
Fe-Bi film	1	490	0.5 M BBS	8
Cu-Bi/FTO	10	810	0.2 M BBS	9
CuO/FTO	0.1	430	0.1 M KBi	10
Ni-Bi film/FTO	1	540	0.5 M K-Bi	11
NiO_x-Bi	1	650	0.5 M K-Bi	12
NiO_x-Fe-Bi	5	552	0.5 M K-Bi	12
Co_3O_4 nanorod	1	385	0.1 M K-Bi	13
Co_3O_4/MWNTs	1	400	0.1 M PBS	14
Fe-Ci/FTO	10	560	0.2 M CBS	15
Fe-based film	1	480	0.1 M PBS	16

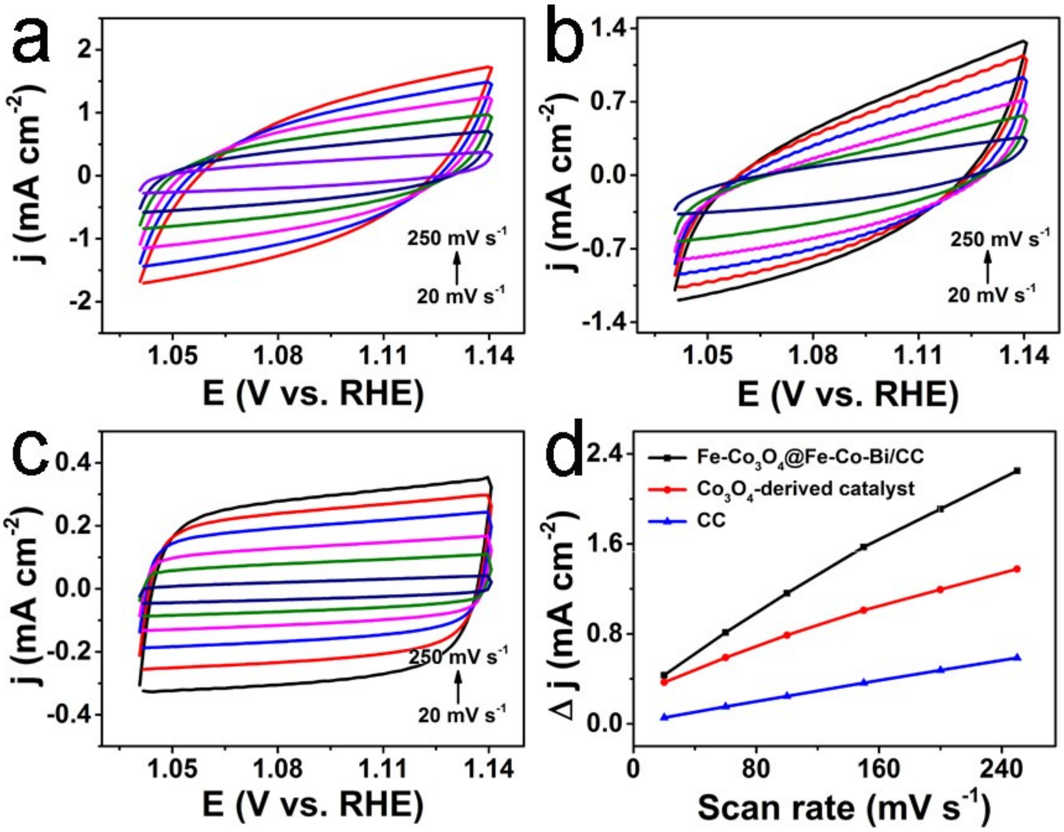

Fig. S5. CVs for (a) Fe-Co_3O_4@Fe-Co-Bi/CC, (b) Co_3O_4-derived catalyst and (c) bare CC in the non-faradaic capacitance current range at scan rates of 20, 60, 100, 150, 200 and 250 mV s^{-1}. (d) Corresponding capacitive currents at 1.09 V vs. RHE as a function of scan rate for Fe-Co_3O_4@Fe-Co-Bi/CC, Co_3O_4-derived catalyst and bare CC in 0.1 M K-Bi.

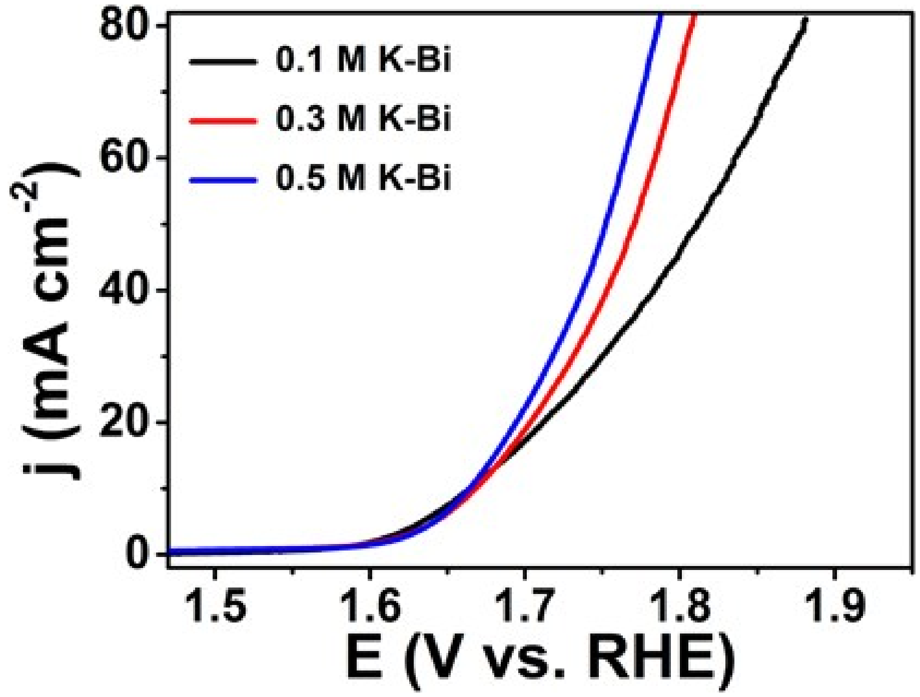

Fig. S6. LSV curves for Fe-Co_3O_4@Fe-Co-Bi/CC in 0.1, 0.3, and 0.5 M K-Bi for OER.

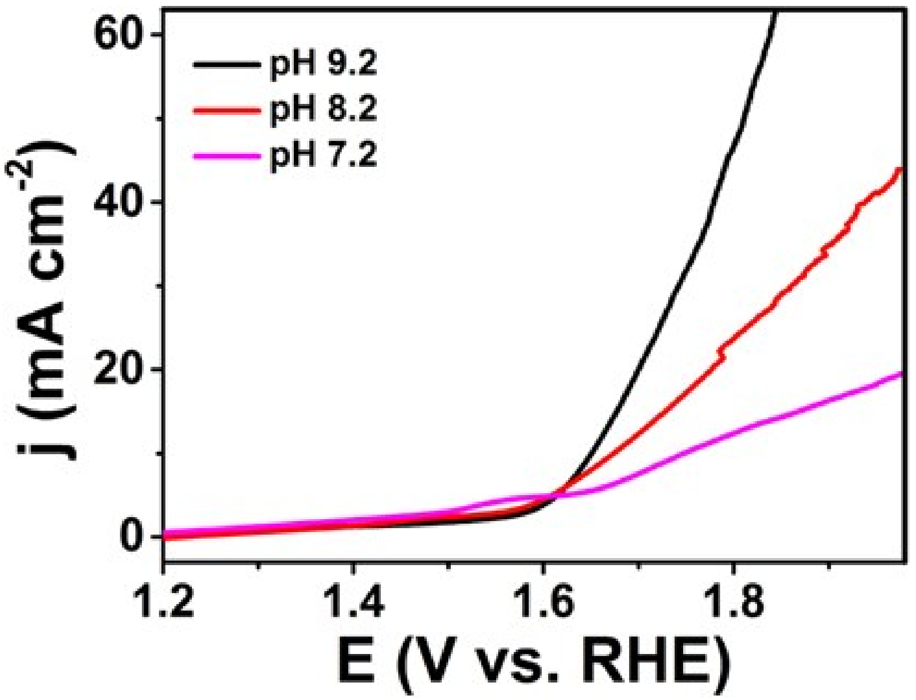

Fig. S7. LSV curves for Fe-Co_3O_4@Fe-Co-Bi/CC in 0.1 M K-Bi under different pH values for OER.

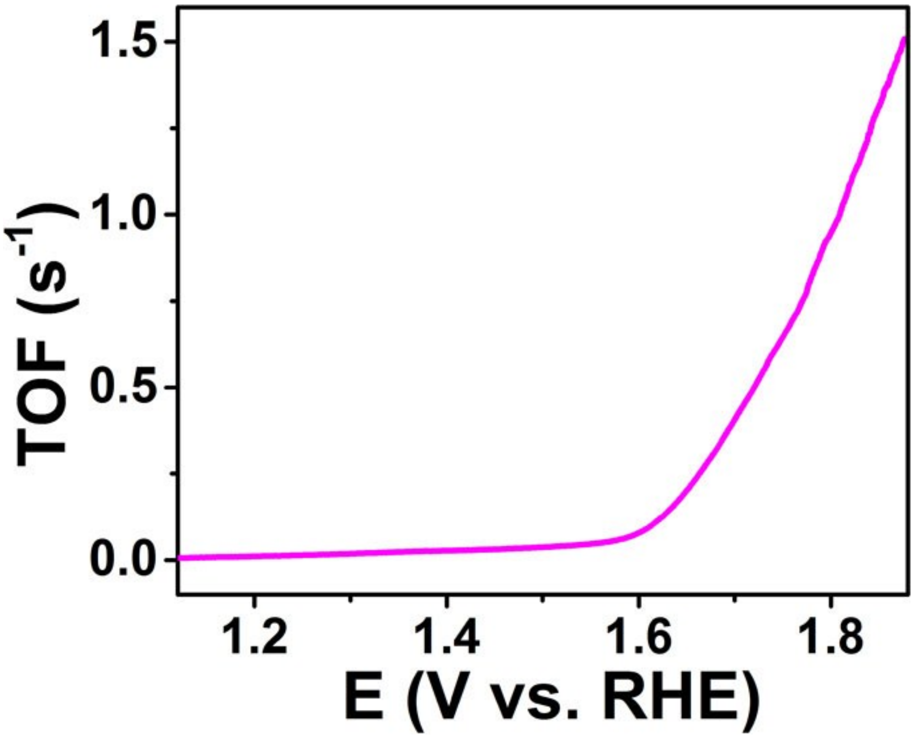

Fig. S8. Plot of TOF vs. potential for Fe-Co_3O_4@Fe-Co-Bi/CC.

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