Electronic Supplementary Information

Experimental Section

Materials: Ti mesh was provided by Hangxu Filters Flag Store, Hengshui, Hebei. 50% manganese nitrate ($Mn(NO_3)_2$) solution and cobaltous nitrate ($Co(NO_3)_2 \cdot 6H_2O$) were purchased from Aladdin Ltd. in Shanghai. Ammonium (NH_4F) and urea was provided by Beijing Chemical Works. Ammonium sulfate ($(NH_4)_2SO_4$), sodium hypophosphite (NaH_2PO_2), sodium citrate ($Na_3C_6H_5O_7$), nitric acid (HNO_3) and ethanol were purchased from Tianjin Chemical Corporation. $RuCl_3 \cdot 3H_2O$ and nafion (5 wt %) were bought from Sigma-Aldrich Chemical Reagent Co., Ltd. All chemical regents were used as received without further purification. Deionized water was made by the Millipore system and used in all experimental process.

Preparation of $MnCo_2O_4$/Ti and Mn-Co-P@$MnCo_2O_4$/Ti: Typically, deionized water (70 ml) containing 1.165 g $Co(NO_3)_2 \cdot 6H_2O$ (4 mmol), 0.7158 g $Mn(NO_3)_2$ (2 mmol), 0.37 g NH_4F (10 mmol) and 1.44 g urea (24 mmol) into a 100 mL beaker. Then, the solution stirs for 15 minutes, and transferred the clear solution and Ti mesh (2 cm × 4 cm) to a 100 ml Teflon-lined autoclave. The autoclave was sealed and heat at 120 °C for 5 h in an electric oven. The resulting precursor was washed with deionized water for several times and further annealed at 300 °C in air to convert into $MnCo_2O_4$/Ti. To realize the transformation of $MnCo_2O_4$/Ti to Mn-Co-P@$MnCo_2O_4$/Ti, $MnCo_2O_4$ nanowires array was treated at -0.95 V (vs. SCE) in sodium hypophosphite solution for 1400 s.

Synthesis of RuO_2: RuO_2 was prepared in accordance with previous report.[1] Firstly, 2.61 g $RuCl_3 \cdot 3H_2O$ was dispersed in 100 mL distilled water and stirred for 10 minutes at 100 °C. Then 1.0 ml NaOH (1.0 M) was added into the above solution. And the mixture was under 100 °C for another 45 minutes. After cool to room temperature, the mixture was centrifuged to collect the precipitation, further dried at 80 °C for 12 h. The dried precipitation was annealed at 300 °C in Ar atomosphere to achieve RuO_2.

Characterizations: The XRD patterns were obtained from a LabX XRD-6100 X-ray diffractometer with Cu Kα radiation (40 kV, 30 mA) of wavelength 0.154 nm (SHIMADZU, Japan). Scanning electron microscopy (SEM) measurements were performed on a HITCHI S-4800 scanning electron microscope at an accelerating voltage of 25 kV. Transmission electron microscopy (TEM) measurements were made on a Zeiss Libra 200FE transmission electron microscope operated at 200 kV. X-ray photoelectron spectrometer (XPS) measurements were performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source. ICP-AES analysis was performed on ThermoScientific IAP6300.

Electrochemical measurements: Electrochemical measurements were performed with a CHI 660E electrochemical analyzer (CH Instruments, Inc., Shanghai). In a typical three-electrode system, the $MnCo_2O_4$/Ti or Mn-Co-P@$MnCo_2O_4$/Ti was used as the working electrode (0.5 cm × 0.5 cm), a graphite rod as the counter electrode and SCE as the reference electrode. To prepare RuO_2 loaded electrodes, 20 mg RuO_2 and 10 μL 5 wt% Nafion solution were dispersed in 1 mL 1:1 v water/ethanol solvent by 30 min sonication to form an ink finally. The potentials reported in this work were converted to the RHE with the following equation: E (RHE) = E (SCE) + (0.24 + 0.0591 pH) V. Linear sweep voltammetry test was performed at a scan rate of 5 mV s^{-1} at room temperature (~25 °C). To calculate turnover frequency (TOF), cyclic voltammetry (CV) tests of $MnCo_2O_4$/Ti and Mn-Co-P@$MnCo_2O_4$/Ti were conducted with scanning rates of 10, 20, 30, 40, 50, and 60 mV s^{-1}, respectively.

TOF calculation: To calculate TOF, the surface concentration of active sites related to the redox Mn and Co species was first obtained. According to the electrochemical CV curves (Fig. 4A), the oxidation peak current of redox species presents linear change on scan rates (Fig. 4B). The slope of the line can be calculated using the following equation:

$$slope = \frac{n^2 F^2 A \tau_0}{4RT}$$

Where n is the number of electrons transferred, F is Faraday's constant, A is the surface area of the electrode, τ_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. TOF values can be finally calculated based on the formula:

$$TOF = \frac{JA}{4FM}$$

J is the current density at 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 for active sites.

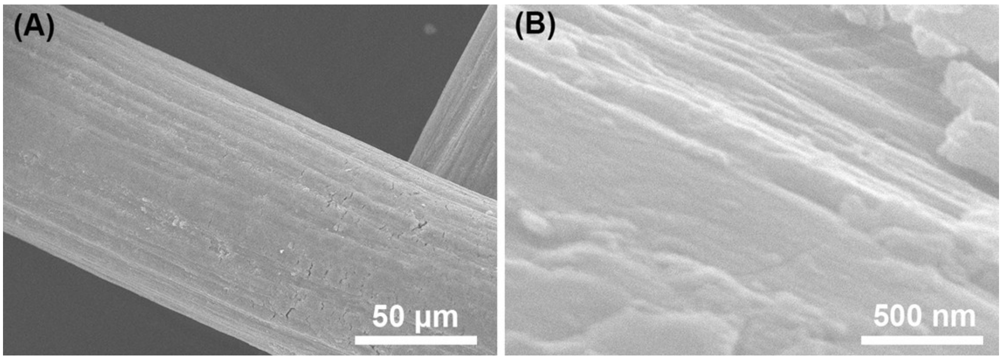

Fig. S1. SEM images of bare Ti mesh.

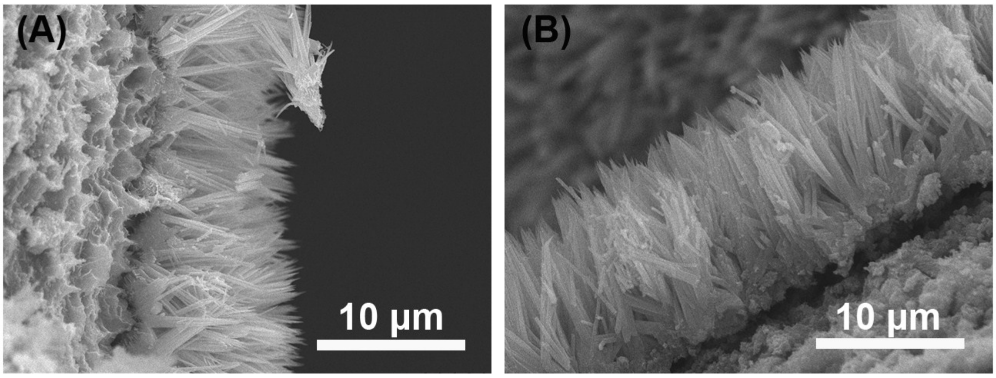

Fig. S2. Cross-section SEM images of (A) $MnCo_2O_4$/Ti and (B) Mn-Co-P@$MnCo_2O_4$/Ti.

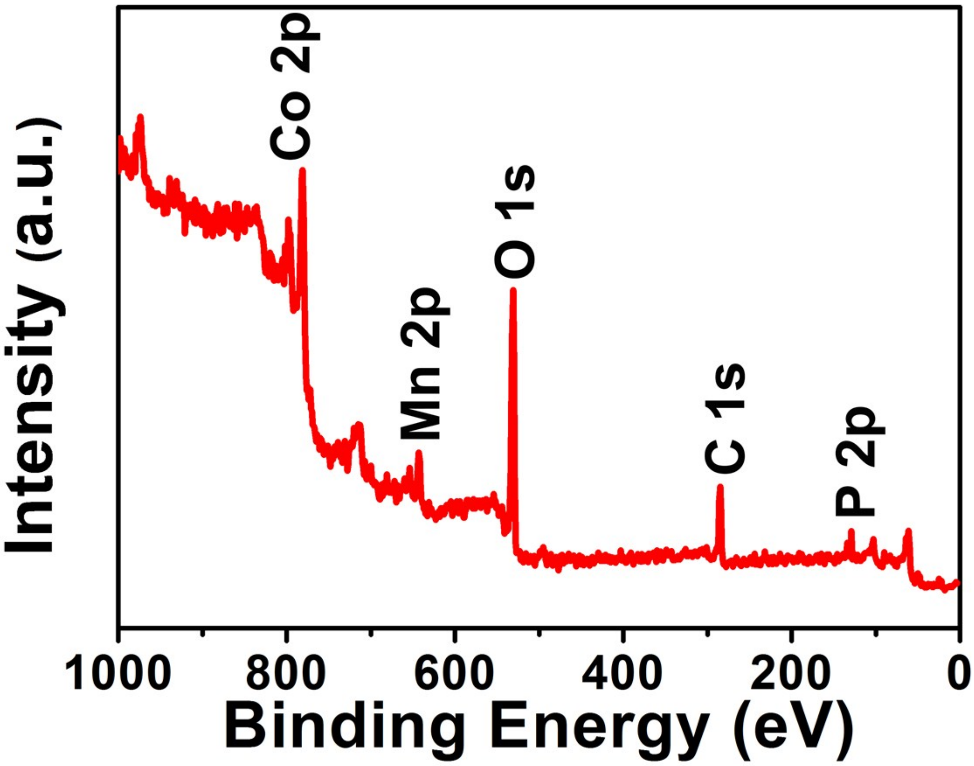

Fig. S3. XPS survey spectrum for Mn-Co-P@$MnCo_2O_4$.

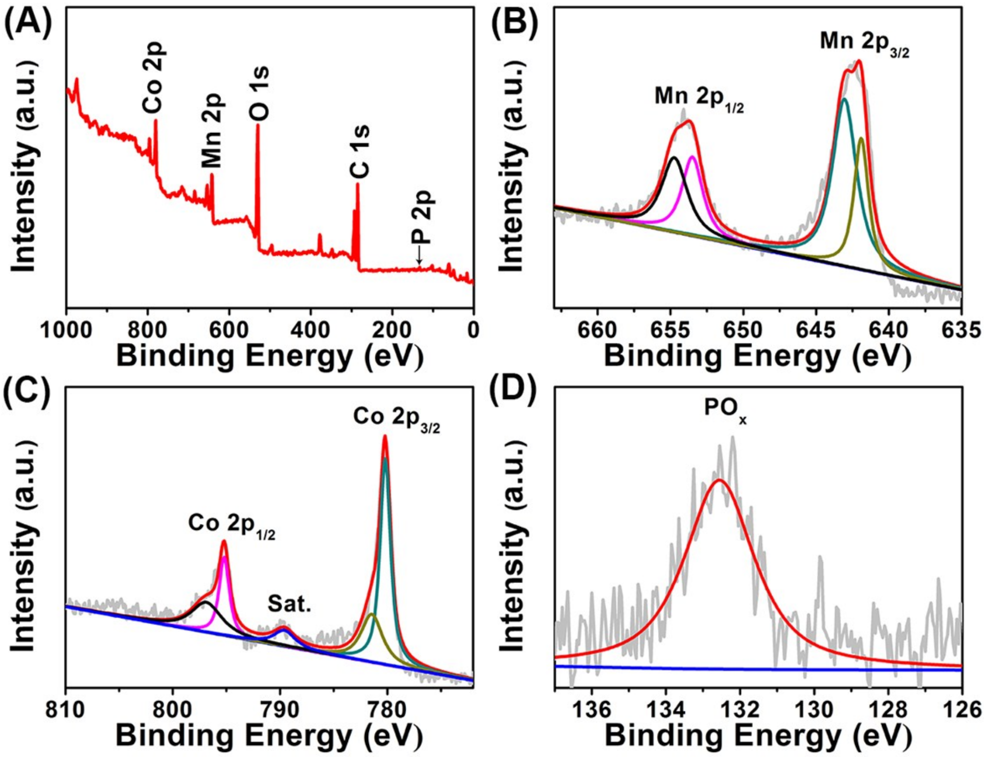

Fig. S4. (A) XPS survey spectrum for Mn-Co-P@MnCo$_2$O$_4$. XPS spectra of Mn-Co-P@MnCo$_2$O$_4$ in the (B) Mn 2p, (C) Co 2p, and (D) P 2p regions after OER electrolysis.

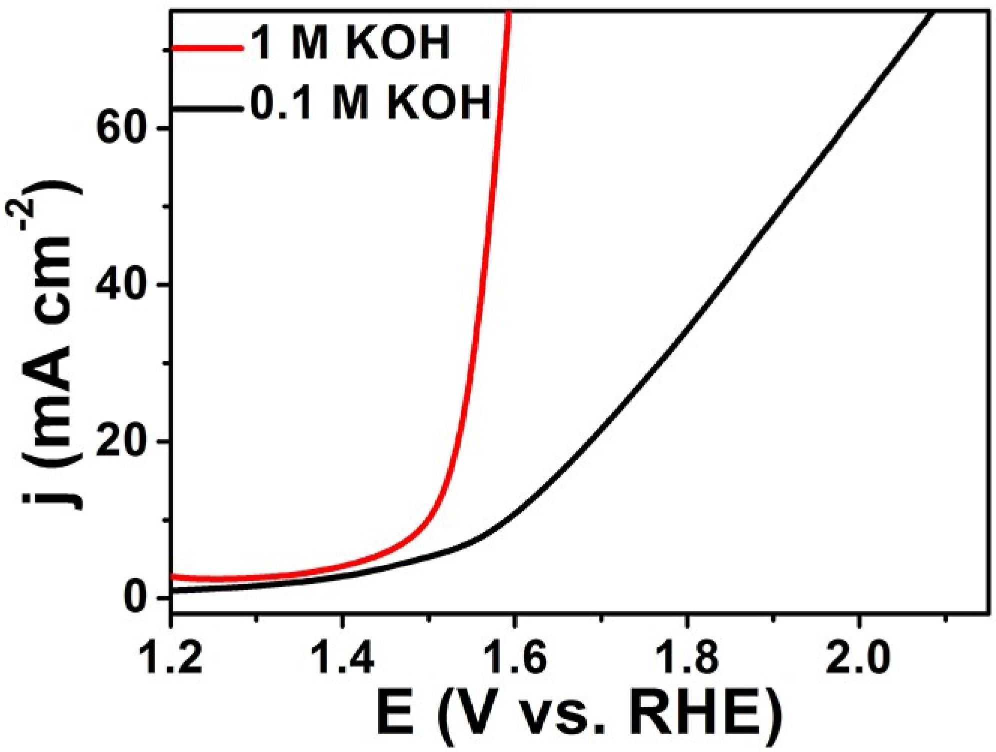

Fig. S5. LSV curves for Mn-Co-P@$MnCo_2O_4$/Ti in 0.1 M KOH and 1.0 M KOH with a scan rate of 5 mV s^{-1}.

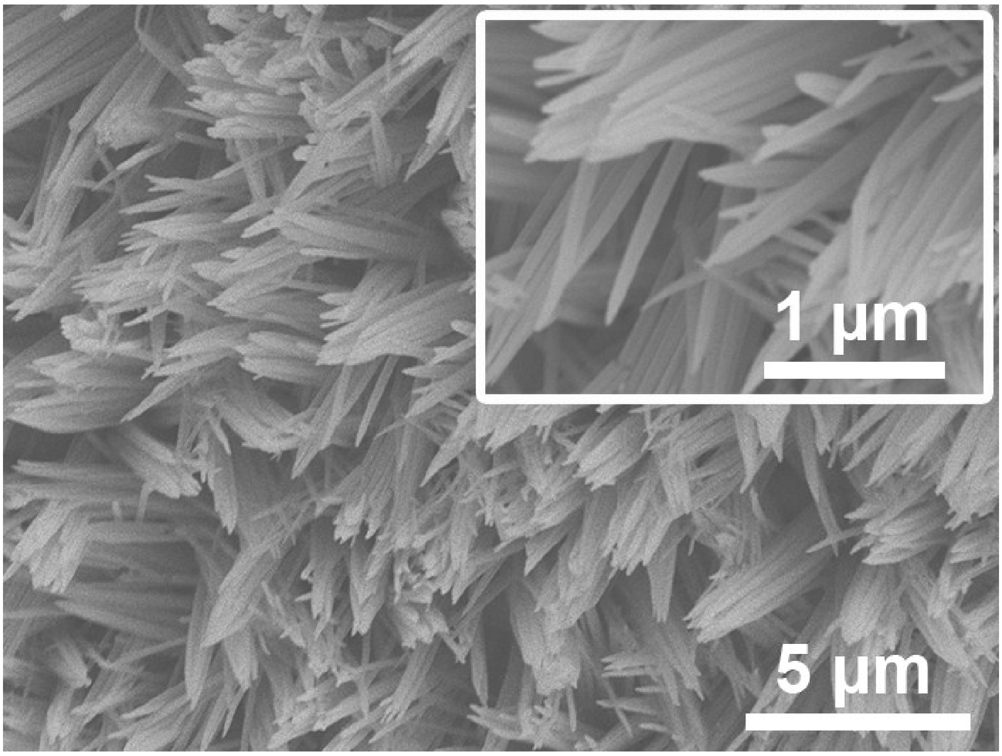

Fig. S6. SEM images of Mn-Co-P@$MnCo_2O_4$/Ti after long-term electrolysis.

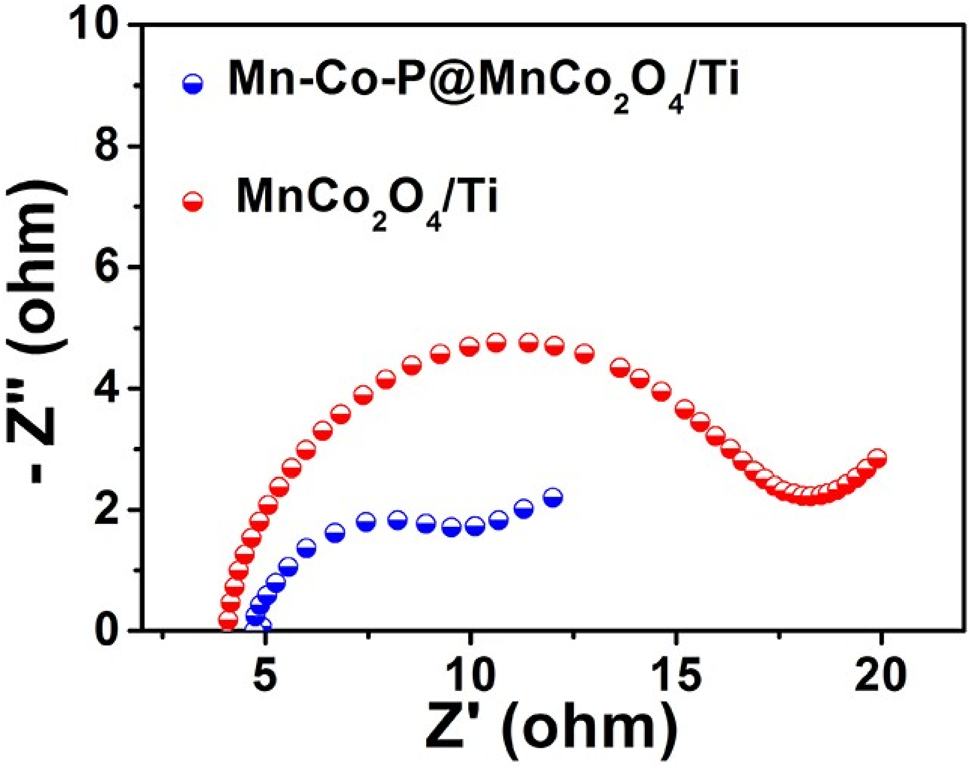

Fig. S7. Nyquist plots of Mn-Co-P@$MnCo_2O_4$/Ti and $MnCo_2O_4$/Ti.

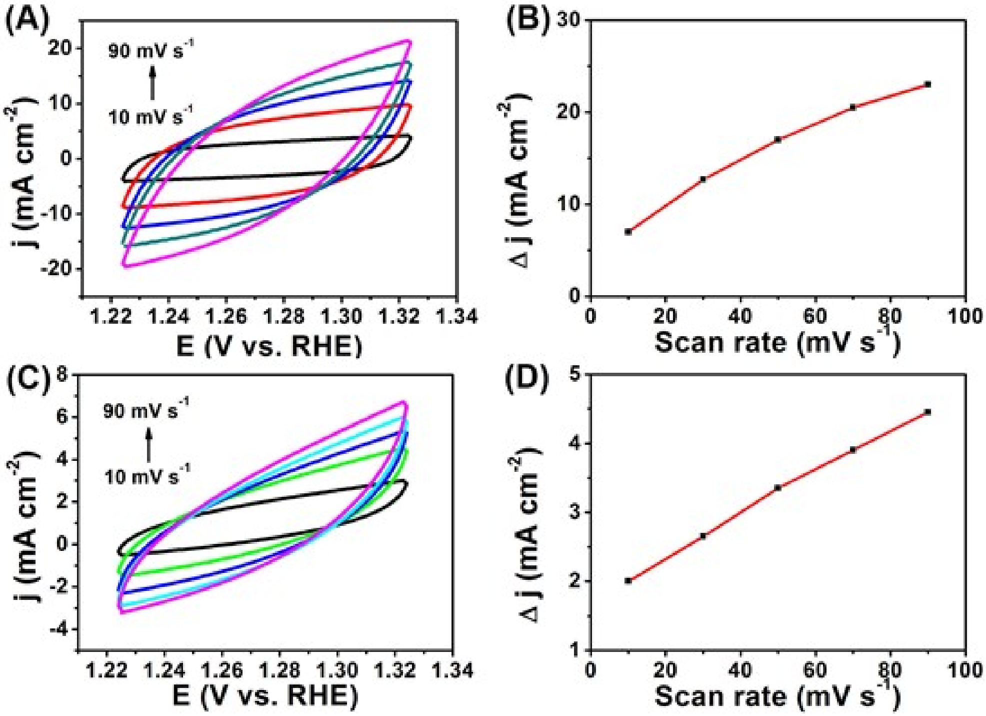

Fig. S8. CVs for (A) Mn-Co-P@MnCo$_2$O$_4$/Ti and (C) MnCo$_2$O$_4$/Ti in the non-faradaic capacitance current range at scan rates of 10, 30, 50, 70 and 90 mV s^{-1}. Corresponding capacitive currents at 1.27 V vs. RHE as afunction of scan rate for (B) Mn-Co-P@MnCo$_2$O$_4$/Ti and (D) MnCo$_2$O$_4$/Ti in 1.0 M KOH, respectively.

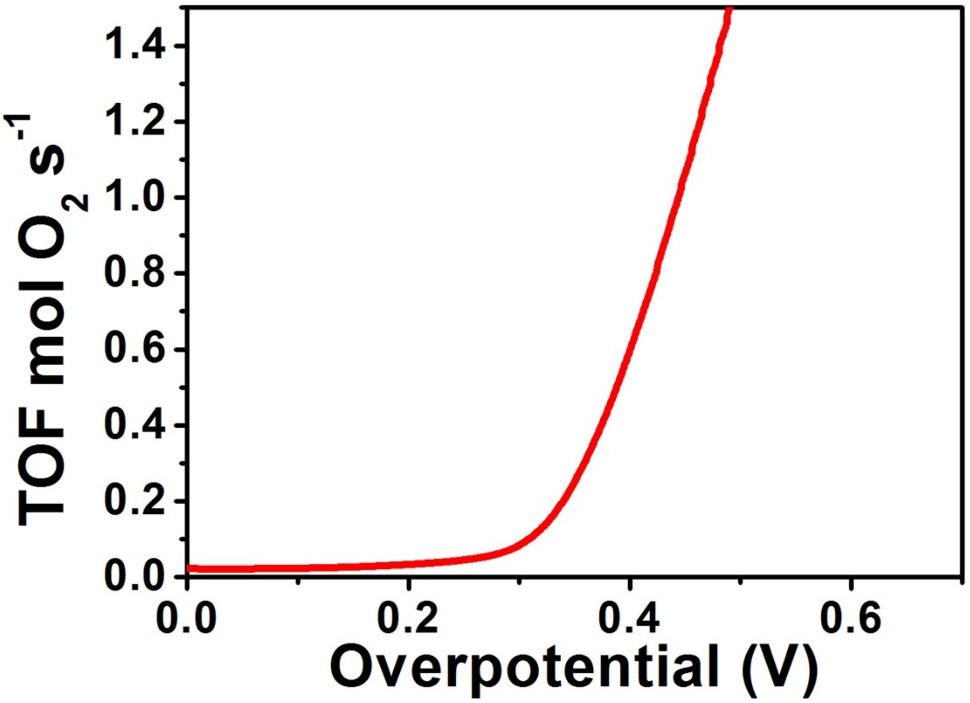

Fig. S9. Plot of TOF vs. overpotential for Mn-Co-P@$MnCo_2O_4$/Ti.

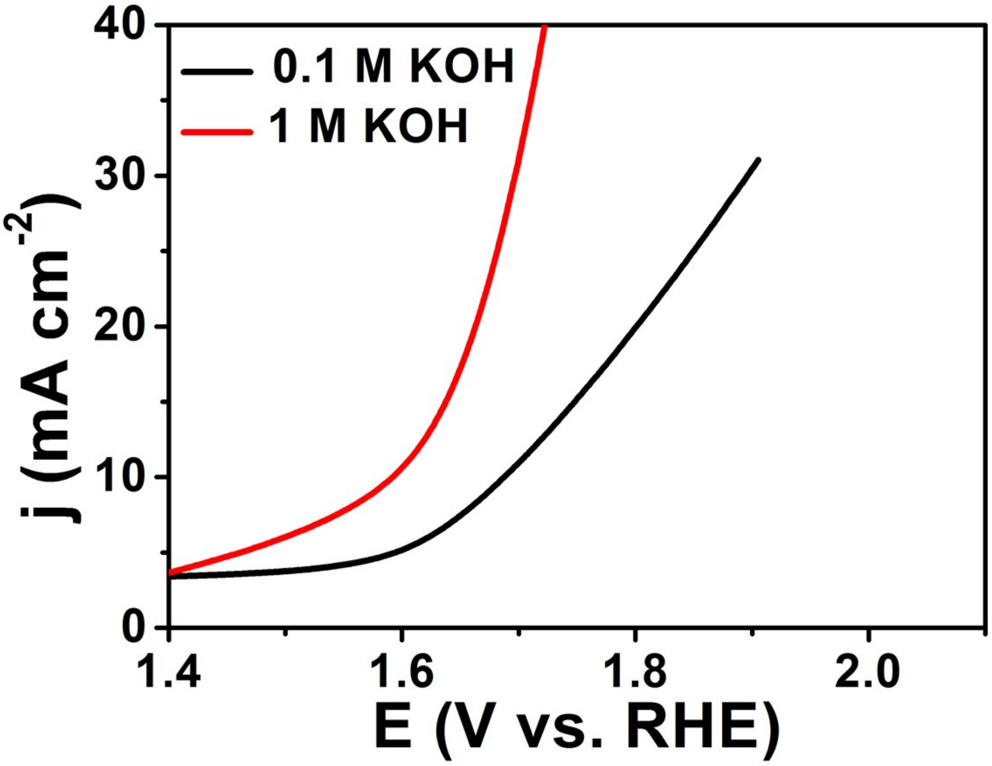

Fig. S10. LSV curves for $MnCo_2O_4$/Ti in 0.1 M KOH and 1.0 M KOH with a scan rate of 5 mV s^{-1}.

Table S1. ICP-AES data for Mn-Co-P@$MnCo_2O_4$/Ti at different electrochemical transformation treatment time.

Element	**800 s**	**1400 s**	**2000 s**
P (mg cm^{-2})	0.077	0.080	0.095

Table S2. Comparison of OER performance for Mn-Co-P@$MnCo_2O_4$/Ti with other non-noble-metal electrocatalysts in alkaline media.

Catalyst	j (mA cm^{-2})	η (mV)	Electrolyte	Refs.
Mn-Co-P@$MnCo_2O_4$/Ti	10	269	1.0 M KOH	This work
	10	360	0.1 M KOH	
CoP	10	281	1.0 M KOH	2
a-CoSe/Ti	10	292	1.0 M KOH	3
NCPP	10	320	1.0 M KOH	4
CoP NR/C	10	320	1.0 M KOH	5
CoMnP nanoparticles	10	330	1.0 M KOH	6
$CoMoO_4$ nanorod	10	343	1.0 M KOH	7
Co-P film	10	345	1.0 M KOH	8
CoMn-LDH	10	324	1.0 M KOH	9
Co_3O_4 NCs	16.5	350	1.0 M KOH	10
Co_3O_4 MNTs	10	353	0.1 M KOH	11
Co-P/NC	10	319	1.0 M KOH	12
Fe/mCo_3O_4	10	380	1.0 M KOH	13
$NiCo_2O_4$-δ	10	390	1.0 M KOH	14
$Mn_{0.1}Ni_1$	10	360	0.1 M KOH	15
CMO/20N-rGO	10	450	1.0 M KOH	16
Mn_3O_4/$CoSe_2$	10	450	0.1 M KOH	17
α-MnO_2	10	490	0.1 M KOH	18
dp-$MnCo_2O_4$/CNT	10	>440	0.1 M KOH	19
$ZnCo_2O_4$	10	390	1.0 M KOH	20
MCO@PPy	10	>500	0.1 M KOH	21

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