Electronic Supplementary Information

Experimental section

Materials: Ti mesh (TM) was provided by Hangxu Filters Flag Store, Hengshui, Hebei. 50% manganese nitrate (Mn(NO₃)₂) solution and Cobaltous nitrate (Co(NO₃)₂· $6H_2O \ge$ 98.5%) was purchased from Aladdin Ltd. in Shanghai. Ammonium (NH₄F \ge 96%) and urea (\ge 99%) were purchased from Aladdin Ltd. (Shanghai, China). RuCl₃· $3H_2O$ (\ge 43%)were bought from Sigma-Aldrich Chemical Reagent Co., Ltd. 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 MnCo₂O₄ NA/TM and MnCo₂S₄ NA/TM: MnCo-hydroxide nanoarray was prepared as follows. 2 mmol Mn(NO₃)₂·4H₂O (0.72 g), 4 mmol $Co(NO_3)_2 \cdot 6H_2O$ (1.16 g), 24 mmol urea (1.45 g) and 10 mmol NH₄F (0.37 g) were dissolved in 70 mL distilled water. After gently stirring for 10 min, the clear solution was transferred to a 100 mL Teflon-lined stainless steel autoclave and a piece of Ti mesh $(2 \times 4 \text{ cm})$ was immersed into the autoclave contained solution. Ti mesh 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 5 h in an electric oven. After the autoclave cooled down to room temperature, the resulting MnCo precursor was taken out and washed with water and ethanol several times, followed by drying at 60 $^{\circ}$ C. Subsequently, the sample was annealed at 300 $^{\circ}$ C in air for 2 h to obtain MnCo₂O₄ NA/TM. To prepare MnCo₂S₄ NA/TM, MnCo₂O₄ NA/TM and 2 g S powder were put into two separate porcelain boat, and one of the porcelain boat with S powder at the upstream side of the furnace, subsequently, the sample were heated at 400 °C for 1 h in a static Ar atmosphere, and then naturally cooled to ambient atmosphere. According to XRD, size of coherently diffracting domains for MnCo₂O₄ and MnCo₂S₄ are 11.6 and 19.3 nm, respectively. The yields of MnCo precursor, MnCo₂O₄, and MnCo₂S₄ are 87.2%, 84.8%, and 83.3%, respectively.

Synthesis of RuO_2 : RuO_2 was prepared according to previous publication. Briefly, 2.61 g of $RuCl_3 \cdot 3H_2O$ and 30.0 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. For a typical synthesis of RuO₂/TM electrode, 50 mg RuO₂ was dispersed in 1 mL ethane/water (v:v = 1:1) solution with sonication for 30 min. Then 8.9 μ L catalytic inks were dropped on Ti mesh (0.5 × 0.5 cm), and dried at 80 °C for 4 h.

Characterizations: Powder X-ray diffraction (XRD) patterns were performed using a RigakuD/MAX 2550 diffractometer with Cu K α 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. Xray 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. MnCo₂S₄NA/TM was used as the working electrode. Graphite plate, and an Hg/HgO 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 (Hg/HgO) + (0.098 + 0.059 pH) V. In this communication, all the data are measured several times.



Fig. S1. EDX spectrum of $MnCo_2S_4 NA/TM$.



Fig. S2. Cross-section SEM image of $MnCo_2S_4 NA/TM$.



TEM image of MnCo₂S₄.

S3.

Fig.



Fig. S4. XPS spectra of $MnCo_2S_4$ in the (a) Mn 2p, (b) Co 2p, and (c) S 2p regions after OER electrolysis.

Fig. S5. LSV curves of $MnCo_2S_4$ NA/TM before and after 500 cycles.



Fig. S6. Cyclic voltammograms (CVs) of (a) $MnCo_2S_4$ NA/TM and (b) $MnCo_2O_4$ NA/TM at different scan rates increasing from 10 to 80 mV s⁻¹ in 1.0 M KOH. Oxidation peak current density versus scan rate plots for (c) $MnCo_2S_4$ NA/TM and (d) $MnCo_2O_4$ NA/TM.



Plots of TOF vs. potential for $MnCo_2S_4$ NA/TM and $MnCo_2O_4$ NA/TM.



LSV curves for $MnCo_2S_4$ NA/TM in KOH with different concentrations.

Fig. S9. the amount of O_2 theoretically calculated and experimentally measured versus time for evolved oxygen of $MnCo_2S_4$ NA/TM

Catalyst	<i>j</i> (mA cm ⁻²)	η (mV)	Loading (mg cm ⁻²)	Electrolyte	Ref.
MnCo ₂ S ₄ NA/TM	50	325	1.78	1.0 M KOH	This work
NiCo ₂ S ₄ /CC	50	310	0.43	1.0 M KOH	1
Co ₃ O ₄ NCs	50	420	0.35	1.0 M KOH	2
Co-P	50	420	2.47	1.0 M KOH	3
NiCo LDH	50	431	0.17	1.0 M KOH	4
NiCo ₂ O ₄	50	435	0.3	1.0 M KOH	5
Mn ₃ O ₄ /Ni foam	50	350		1.0 M KOH	6
CoMoO ₄	50	385		1.0 M KOH	7
NiCo ₂ O ₄	50	380	0.2	1.0 M NaOH	8
amorphous CoSe/Ti	50	355	3.8	1.0 M KOH	9
ECT-CoO nanosheets	50	337		1.0 M KOH	10
NiCo ₂ O ₄ NNs	20	807	0.53	1.0 M KOH	11
NixCo _{3-x} O ₄ NA	10	370	3	1.0 M KOH	12
Ni _{0.33} Co _{0.67} S ₂	10	330	0.3	1.0 M KOH	13
5.9 nm Co ₃ O ₄	10	328	1	1.0 M KOH	14
Ni-doped Co ₃ O ₄	10	530	0.14	1.0 M KOH	15
Co ₃ S ₄ nanosheet	10	355		0.1 M KOH	16
mesoporous Co ₃ O ₄	10	525	0.13	0.1 M KOH	17
Mn ₃ O ₄ /CoSe ₂	10	450	0.2	0.1 M KOH	18
NiCo ₂ S ₄ @N/S- rGO	10	470	0.283	0.1 M KOH	19

Table S1. Comparison of OER performance for $MnCo_2S_4$ NA/TM with other non-noble-metal electrocatalysts in alkaline media.

$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}$	10	362		0.1 M KOH	20
Co ₃ O ₄ /N-	10	210			21
rmGO/NF	10	510			<i>2</i> I
Crumpled	10	240			22
graphene CoO	10	340			22
CoMoO ₄ nanorod	10	343	0.42	1.0 M KOH	23
NiCo-LDH/carbon	10	267	0.17		24
paper	10	307			24
CoMn-LDH	10	350	0.142	1.0 M KOH	25
Co-S/Ti mesh	10	361		1.0 M KOH	26

References

- 1. D. Liu, Q. Lu, Y. Luo, X. Sun and A. M. Asiri, Nanoscale, 2015, 7, 15122–15126.
- S. Du, Z. Ren, J. Zhang, J. Wu, W. Xi, J. Zhu and H. Fu, *Chem. Commun.*, 2015, 51, 8066–8069.
- N. Jiang, B. You, M. Sheng and Y. Sun, *Angew. Chem., Int. Ed.*, 2015, 127, 6349–6352.
- H. Liang, F. Meng, C. A. Miguel, L. Li, A. Forticaux, L. Xiu, Z. Wang and S. Jin, Nano Lett., 2015, 15, 1421–1427.
- Z. Peng, D. Jia, A. Al-Enizi, A. Elzatahry and G. Zheng, *Adv. Energy Mater.*, 2015, 5, 1402031.
- M. Yu, Y. Li, S. Yang, P. Liu, L. Pan, L. Zhang and H. Yang, J. Mater. Chem. A, 2015, 3, 14101–14104.
- 7. M. Yu, L. Jiang and H. Yang, Chem. Commun., 2015, 51, 14361–14364.
- 8. R. Chen, H. Wang, J. Miao, H. Yang and B. Liu, Nano Energy, 2015, 11, 333–340.
- T. Liu, Q. Liu, A. M. Asiri, Y. Luo and X. Sun, *Chem. Commun.*, 2015, 51, 16683– 16686.
- W. Chen, H. Wang, Y. Li, Y.Liu, J. Sun, S. Lee, J. Lee and Y. Cui, ACS Cent. Sci., 2015, 1, 244–251.
- 11. H. Shi and G. Zhao, J. Phys. Chem. C., 2014, 118, 25939-25946.
- 12. Y. Li, P. Hasin and Y. Wu, Adv. Mater., 2010, 22, 1926–1929.
- Z. Peng, D. Jia, A. M. Al-Enizi, A. A. Elzatahry and G. Zheng, *Adv. Energy Mater.*, 2015, 5, 1402031.
- A. J. Esswein, M. J. McMurdo, P. N Ross, A. T. Bell and T. D. Tilley, J. Phys. Chem. C, 2009, 113, 15068–15072.
- X. Zou, J. Su, R. Silva, A. Goswami, B. R. Sathe and T. Asefa, *Chem. Commun.*, 2013, 49, 7522–7524.
- Y. Liu, C. Xiao, M. Lyu, Y. Lin, W. Cai, P. Huang, W. Tong, Y. Zou and Y. Xie, Angew. Chem., Int. Ed., 2015, 54, 11231–11235.
- H. Tüysüz, Y. J. Hwang, S. B. Khan, A. M. Asiri and P. Yang, *Nano Res.*, 2013, 6, 47–54.

- M. Gao, Y. Xu, J. Jiang, Y. Zheng and S. Yu, J. Am. Chem. Soc., 2012, 134, 2930– 2933.
- 19. Q. Liu, J. Jin and J. Zhang, ACS Appl. Mater. Interfaces., 2013, 5, 5002-5008.
- J. Suntivich, K. J. May, H. A. Gasteiger, J. B. Goodenough and Y. Shao-Horn, Science, 2011, 334, 1383–1385.
- Y. Liang, Y. Li, H. Wang, J. Zhou, J. Wang, T. Regier and H. Dai, *Nat. Mater.*, 2011, 10, 780–786.
- 22. S. Mao, Z. Wen, T. Huang, Y. Hou and J. Chen, *Energy Environ. Sci.*, 2014, 7, 609–616.
- 23. X. Liu, Y. Yang and S. Guan, Chem. Phys. Lett., 2017, 675, 11-14.
- H. Liang, F. Meng, M. Cabán-Acevedo, L. Li, A. Forticaux, L. Xiu, Z. Wang and S. Jin, *Nano Lett.*, 2015, 15, 1421–1427.
- 25. F. Song and X. Hu, J. Am. Chem. Soc., 2014, 136, 16481–16484.
- T. Liu, Y. Liang, Q. Liu, X. Sun, Y. He and A. M. Asiri, *Electrochem. Commun.*, 2015, 60, 92–96.