Electronic Supplementary Material

NiFeRuO_x nanosheets on Ni foam as an electrocatalyst for efficient overall alkaline seawater splitting

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Fig. S1 Morphologies of NiFeRuO_x/NF (a, b) without calcination, calcined at (c, d) 250 °C, (e, f) 300 °C and (g, h) 350 °C with different magnifications.



Fig. S2 The XRD pattern of as-synthesized NiFeRuO_x without NF.



Fig. S3 The XRD patterns of samples calcined at 250 °C and 350 °C. (a) NiFeRuO_x/NF (b) materials scraped from the foam (c) without NF.

| Ru content/mg L-1 | Fe content/mg L ⁻¹ | Ni content/mg L ⁻¹ | Ru/(Ru+Fe+Ni) atomic ratio |
|-------------------|-------------------------------|-------------------------------|----------------------------|
| 29.5 | 29.0 | 861.3 | 1.9% |

Ni 2p O KLL Fe 2p O 1s C 1s & Ru 3d Ni 3p 1200 1000 800 600 400 200 0 Binding energy/(eV)

Fig. S4 Wide-scanning XPS spectrum of NiFeRuO_x/NF.



Fig. S5 The C_{dl} of NiFeRuO_x/NF, commercial Pt/C/NF and bare NF for HER.

The C_{dl} were obtained from the linear relationship between the capacitive current (ΔJ) and scan rates.

For the calculation of ECSA, the value of specific capacitance for a flat surface (1 cm^2) is assumed as 40 μ F cm⁻². Note that NF was used as the support and its specific capacitance is much larger than

 Table S1 The metal contents in NiFeRuO_x/NF detected by ICP-AES.

that of a flat surface. Therefore, here the NF was considered as the standard [1]. The ECSA is calculated according to the following equation [2, 3]:

$$A_{ECSA} = \frac{C_{dl} - electrocatalyst \ (mF \ cm^{-2})}{C_{dl} - bare \ Ni \ foam \ (mF \ cm^{-2}) \ per \ ECSA \ (cm^{-2})}$$

Taking NiFeRuO_x/NF as an example, upon the HER, it can be calculated as:

$$A_{ECSA} = \frac{14.5 \ mF \ cm^{-2}}{1.2 \ mF \ cm^{-2} \ per \ ECSA} = 12.1 \ cm_{ECSA}^2$$

| fab.S2 The ECSA values of electrocatalysts normalized by Cdl. | | | |
|----------------------------------------------------------------------|-------------|---------------------------------|---------|
| ECSA for HER/(cm ² _{ECSA}) | NiFeRuOx/NF | commercial PtC/NF | bare NF |
| | 12.1 | 19.7 | 1 |
| ECSA for OER/(cm ² _{ECSA}) | NiFeRuOx/NF | commercial RuO ₂ /NF | bare NF |
| | 3.4 | 1.5 | 1 |



Fig.S6 Nyquist plots of NiFeRuO_x/NF, commercial Pt/C/NF and bare NF for HER.

Tab.S3 The mass content of Ru in NiFeRuO_x/NF and Pt commercial Pt/C/NF.

| | NiFeRuOx/NF | commercial PtC/NF |
|--------------------------|-------------|-------------------|
| Mass content of Ru or Pt | 0.472 mg | 0.2 mg |

According to ICP, the mass of Ru in NiFeRuO_x/NF ($1 * 1 \text{ cm}^2$) is calculated to 0.472 mg. According to the preparation of commercial Pt/C/NF (in 2.4 Electrochemical measurements), the mass of Pt loaded on the NF was 0.2 mg (5 mg/mL * 200 µL * 20 wt.%). Considering the price of Ru is about 1/3 of Pt [4], we can estimate the price of Pt in commercial Pt/C/NF is 1.27 times as much as that of Ru in NiFeRuO_x/NF. Moreover, NiFeRuO_x/NF could perform as a bifunctional electrocatalyst in alkaline simulated seawater.



Fig.S7 The C_{dl} of NiFeRuO_x/NF, commercial RuO₂/NF and bare NF for OER.



Fig.S8 Nyquist plots of NiFeRuO_x/NF, commercial RuO₂/NF and bare NF for OER.



Fig.S9 (a, b) SEM images of 0.02 mmol and 0.1 mmol samples. (c) The XRD patterns of materials scraped from 0.02 mmol and 0.1 mmol samples. Inserted is the samples on NF. (d) The XRD patterns of 0.02 mmol and 0.1 mmol samples without NF. (e) HER and (f) OER polarization curves of 0.02 mmol and 0.1 mmol samples.



Fig.S10 (a) HER and (b) OER polarization curves of NiFeRuO_x/NF calcined at 250 °C. (c) HER and (b) OER polarization curves of NiFeRuO_x/NF calcined at 350 °C.

Tab.S4 Comparison of the electrocatalytic overall water splitting activity of the NiFeRuO_x/NF with the reported electrocatalysts in alkaline media.

| Catalysts | Electrolytes | Cell voltage/V at 10 mA cm ⁻² | References |
|----------------------------------------|----------------------|---------------------------------------------|-------------------------------------|
| NiFeRuO _x /NF | 1 M KOH+3.5 wt.%NaCl | 1.53 | This work |
| Ru ₂ Ni ₂ SNs/C | 1 M KOH | 1.58 | Nano Energy, 2018, 47, 1-7 |
| Ru ₁ Ni ₁ -NCNFs | 1 M KOH | 1.564 | Adv. Sci., 2020, 7, 1901833 |
| RuCo NSs | 1 M KOH | 1.524 | Adv. Energy Mater., 2020, 2002860 |
| Ru/NiFe LDH-F | 1 M KOH | 1.53 | Nanoscale, 2020, 12, 9669-9679 |
| Ru-CoMo/CFP | 1 M KOH | 1.54 | Appl. Surf. Sci., 2021, 541, 148518 |
| RuCoOx | 1 M KOH | 1.54 | Nano Lett., 2021, 21, 9633-9641 |
| NiMoRuO | 1 M KOH | 1.56 | Chem. Eng. J., 2021, 420, 127686 |
| Ru–NiSe ₂ /NF | 1 M KOH | 1.537 | Small, 2022, 18, 2105305 |
| RuO ₂ -C-300 | 1 M KOH | 1.52 | Small, 2022, 18, 2203778 |
| 1D-Cu@Co-CoO/Rh | 1 M KOH | 1.60 | Small, 2021, 17, 2103826 |



Fig.S11 Experimentally collected H₂ (top) and O₂ (bottom) at different times of 0, 10, 20, 30, 40, 50, 60 min.

Tab.S5 The metal contents in NiFeRuO_x/NF after OER stability test detected by ICP-AES.

| Ru content/mg L-1 | Fe content/mg L ⁻¹ | Ni content/mg L ⁻¹ | Ru/(Ru+Fe+Ni) atomic ratio |
|-------------------|-------------------------------|-------------------------------|----------------------------|
| 22.8 | 21.9 | 834.0 | 1.5% |

- Zeng L Y, Sun K A, Wang X B, Liu Y Q, Pan Y, Liu Z, Cao D W, Song Y, Liu S H, Liu C G. Three-dimensional-networked Ni₂P/Ni₃S₂ heteronanoflake arrays for highly enhanced electrochemical overall-water-splitting activity. Nano Energy, 2018, 51: 26-36
- Sun X, Shao Q, Pi Y, Guo J, Huang X. A general approach to synthesise ultrathin NiM (M = Fe, Co, Mn) hydroxide nanosheets as high-performance low-cost electrocatalysts for overall water splitting. Journal of Materials Chemistry A, 2017, 5(17): 7769-7775
- Yang Y Q, Zhang K, Ling H L, Li X, Chan H C, Yang L C, Gao Q S. MoS₂-Ni₃S₂ heteronanorods as efficient and stable bifunctional electrocatalysts for overall water splitting. ACS Catalysis, 2017, 7(4): 2357-2366
- 4. Zhang D, Wang Z, Wu X, Shi Y, Nie N, Zhao H, Miao H, Chen X, Li S, Lai J, et al. Noble metal (Pt, Rh, Pd, Ir) doped Ru/CNT ultra-small alloy for acidic hydrogen evolution at high current density. Small, 2022, 18(3): 2104559