Supporting Information

3D Porous Amorphous γ-CrOOH on Ni Foam as Bifunctional Electrocatalyst for Overall Water Splitting

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EXPERIMENTAL SECTION

Chemicals and Materials:

(NH₄)₂Cr₂O₇ (Beijing Chemical Reagent Co., Ltd., 99.5%), N₂H₄·H₂O (Beijing Chemical Reagent Co., Ltd, 97.0%), hydrochloric acid (Beijing Chemical Reagent Co., Ltd., 99.5%), acetone (Beijing Chemical Reagent Co., Ltd, 99.0%), ethanol (Beijing Chemical Reagent Co., Ltd, 99.0%), potassium hydroxide (KOH, Beijing Chemical Reagent Co., Ltd, 82.0%), Nafion solution (Sigma-Aldrich Co., 5 wt%) and RuO₂ (Shanghai Macklin Biochemical Co., Ltd, 99.9%), IrO₂ (Sigma-Aldrich Co., 99.9%), platinum on carbon (Sigma-Aldrich Co., 99.9%). All the materials in this experiment were used directly without any purification.

Preparation of γ-CrOOH/NF electrode:
In a facile hydrothermal method, 4 mmol of \((\text{NH}_4)_2\text{Cr}_2\text{O}_7\) was added into 80 mL deionized water under stirring. After 30 min, 2 mL of 1 M HCl solution was slowly added to the above solution, followed by the addition of 4 mL of \(\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}\). The solution was continuously stirred for another 30 min and transfer to Teflon-lined autoclave. The Ni foam was put into the mixture and maintained at 120 °C for 12 h. The powder was washed by water and ethanol and dried with vacuum freeze drier. After it was cooled to room temperature, the electrode was ultrasonicated with water and ethanol several times and then dried at 80 °C. The loading of \(\gamma\)-CrOOH was measured using inductively coupled plasma mass spectroscopy (ICP-MS, Thermo XSeries II) by dissolving 1 cm * 1 cm electrode in 100 mL aquaregia. UV-vis diffuse reflectance spectra were collected on a Shimadzu UV-2450 spectrometer using \(\text{BaSO}_4\) as the reference sample. The optical band gaps could be determined by the equation: \(E_g = 1240/\lambda_{\text{max}}\). Where \(E_g\) represents band gap energy, and \(\lambda_{\text{max}}\) is the biggest absorption edge of the samples.

**Preparation of \(\text{Cr}_2\text{O}_3\)/NF electrode:**

The \(\gamma\)-CrOOH/NF electrode was heated to 750 °C for 4 h in Argon atmosphere. And the electrode was prepared.

**Preparation of \(\text{RuO}_2\)/NF, \(\text{IrO}_2\)/NF, Pt/C/NF electrode:**

\(\text{RuO}_2\) (5 mg) was dispersed in a 1 mL mixed solution (490 μL water, 15 μL 5 wt % Nafion solution, and 495 μL ethanol) and then followed by sonication to obtain catalyst ink. Put the catalyst ink (100 μL) on the surfaces of Nickel Foam (area: 1 cm*1 cm). Finally, the electrode was dried at 80 °C overnight. And the method of preparation of \(\text{IrO}_2\)/NF, Pt/C/NF electrode is similar to \(\text{RuO}_2\)/NF. By weighing the mass difference before and after, the loading of catalysts (\(\text{RuO}_2\), \(\text{IrO}_2\), Pt/C) was ca. 0.5 mg cm\(^{-2}\).
**Materials characterization:**

X-Ray diffraction (XRD) was measured via a Phillips X’pert ProMPD diffractometer (CuKα, λ=1.54056 Å, the generator setting was 40 kV and 40 mA). Field emission scanning electronic microscope (FESEM) images was tested via a scanning electron microscope with an acceleration voltage of 10 kV (Hitachi). High-resolution transmission electron microscopy (HRTEM) was measured by a FEI Tecnai F20 transmission electron microscope at an acceleration voltage of 200 kV. The characteristic of the Fourier transform infrared spectroscopy (FT-IR) via a Nicolet-380 Fourier Transform infrared spectrometer. X-Ray photoelectron spectra (XPS) were conducted through ESCALAB 250Xi spectrometer (Thermo Fisher) with Al Kα radiation.

**Electrochemical measurements:**

Electrochemical measurements were performed with a Zennium IM6 station electrochemical analyzer in a standard three-electrode system (a Pt wire as the counter electrode for OER and a carbon rod as the counter electrode for OER, Hg/HgO electrode as the reference electrode, and as-prepared working electrode as the working electrode). The performances were tested in 1.0 M KOH using the linear sweep voltammetry (LSV) curves with a scan rate of 5 mV s⁻¹. The potentials value was converted to the reversible hydrogen electrode (RHE) according to the following formula: \( E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.098 + 0.0591 \times \text{pH} \) and the overpotentials (η) for OER is calculated according to the formula: \( \eta = E_{\text{RHE}} - 1.23 \text{ V} \). Electrochemical impedance spectroscopy (EIS) was measured with an AC voltage with 5 mV amplitude in the frequency range from 0.01 Hz to 100 kHz in a solution of 1.0 M KOH.

**Calculation Methods**

Based on the spin polarized density functional theory (DFT) and the projector augmented wave
(PAW) method as implemented in the Vienna Ab-initio Simulation Package (VASP), the density of states and electrical band structures were calculated by the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA). The effective interaction strengths of different 3d orbitals were set as 5.0 for Cr. A plane-wave basis set was used with kinetic energy cutoff of $E_{\text{cut}}=500$ eV with a K-point grid of $2\times6\times3$ using the Gamma centered method.

Figure S1 Photographs of (a) amorphous $\gamma$-CrOOH and (b) $\text{Cr}_2\text{O}_3$.

Figure S2 XRD of catalysts $\gamma$-CrOOH /NF and $\text{Cr}_2\text{O}_3$/NF.
Figure S3 XRD pattern of Ni foam.

Figure S4 XPS Cr spectra of γ-CrOOH/NF (a), Cr₂O₃/NF.
Figure S5 SEM image of γ-CrOOH/NF at low magnification

Figure S6 HAADF-STEM image and element mapping images for γ-CrOOH/NF.
Figure S7 The digital image of electrolytic cell with electrode.

Figure S8 The LSV curves of hydrogen electrode reactions on Pt wire.

The thermodynamically reversible potential gap between reference electrode and reversible
hydrogen electrode (RHE) was calculated by Nernst equation.

$$E \text{ (RHE)} - E \text{ (HgO/Hg)} = 0.098 \text{ V} + 0.059 \times \text{ pH (1 M KOH)} = 0.926 \text{ V} \quad (1)$$

In order to get the accurate RHE value, the calibration test was conducted in hydrogen saturated 1.0 M KOH (mercury oxide electrodes as reference electrode, Pt wire as working electrode and a graphite electrode). The s LSV was run at rate of 0.1 mV s$^{-1}$. As shown in Figure S8, the current crossed zero for the hydrogen electrode was at -0.926 V with respect to mercury oxide electrodes. The measured and calculated potential gaps between mercury oxide electrodes and RHE are both nearly -0.926 V. So, we have calibrated the potential with respect to RHE in the revised manuscript according to the following equation.

$$E \text{ (RHE)} = E \text{ (HgO/Hg)} + 0.926 \text{ V} \quad (2)$$

**Figure S9** SEM image of $\gamma$-CrOOH/NF after stability test for 20 h in 1.0 M KOH for HER (a) and OER (b).
Figure S10 XPS Cr spectra of the γ-CrOOH/NF for (a) initial electrode, (b) after OER durability tests, (c) after HER durability tests.

Figure S11 CVs of Cr$_2$O$_3$/NF (a) and γ-CrOOH/NF (b) in the non-faradaic capacitance current range at scan rates of 20, 40, 60, 80, and 100 mV s$^{-1}$. 
**Figure S12** the capacitive currents at 1.151 V vs. RHE as a function of scan rate for Cr$_2$O$_3$/NF(a) and γ-CrOOH/NF(b). The determined double-layer capacitance of the system is taken as the average of the absolute value of the slope for the linear fits to the data.

**Figure S13** Nyquist plots of Nickel Foam, Cr$_2$O$_3$/NF and γ-CrOOH/NF electrodes. The inset is an enlarged curve of the high-frequency region for Nickel Foam, Cr$_2$O$_3$/NF and γ-CrOOH/NF.
**Figure S14** UV-visible (UV-vis) diffuse-reflectance spectroscopy (DRS).

**Table S1** the ICP for initial γ-CrOOH/NF and γ-CrOOH/NF after HER and OER test

| Sample | Initial electrode | After HER electrode | After OER electrode |
|--------|-------------------|---------------------|---------------------|
| Cr (μg ml⁻¹) | 2.51 | 2.50 | 2.43 |

**Table S2** Comparison of the electrocatalytic HER activity of γ-CrOOH/NF to other oxide/hydroxide-based HER catalysts in 1 M KOH

| Catalyst | j(mAcm⁻²) | η (mV) | Electrolyte | Ref. |
|----------|-----------|--------|-------------|------|
| γ-CrOOH/NF | 10 | 79 | 1M KOH | This work |
| Cr₂O₃/NF | 50 | 149 | 1M KOH | This work |
| γ-CrOOH/NF | 10 | 183 | 1M KOH | This work |
| γ-CrOOH/NF | 50 | 300 | 1M KOH | This work |
| CoMnCH | 10 | 180 | 1M KOH | J. Am. Chem. Soc. 2017, 139, 8320 |
| NiFeLDH@NiCoP/NF | 10 | 120 | 1M KOH | Adv. Funct. Mater. 2018, 14, 1706847 |
| MoS₂-Ni₃S₂ | 10 | 98 | 1M KOH | ACS Catal. 2017, 7, 2357-2366. |
| (Ni₀.₃₃Fe₀.₆₇)₂P | 50 | 213 | 1M KOH | Adv. Funct. Mater. 2017, 27 1702513. |
| NiCo₂S₄ | 10 | 210 | 1M KOH | Adv Funct Mater. 2016,26 4661-4672 |
| Ni/NiₓMᵧ | 10 | 130 | 1M KOH | Adv. Funct. Mater. 2016,26, 3314 |
### Table S3 Comparison of the electrocatalytic OER activity of γ-CrOOH/NF to other oxide/hydroxide-based OER catalysts in 1 M KOH

| Catalyst                      | j (mAcm⁻²) | η (mV) | Electrolyte | Ref.                                 |
|-------------------------------|------------|-------|-------------|--------------------------------------|
| γ-CrOOH/NF                    | 50         | 334   | 1M KOH      | This work                            |
| Co₃O₄/N-rmGO                  | 72         | 347   | 1M KOH      | Nat. Mater. 2011, 10, 780            |
| NiFeCr LDHs/GC                | 10         | 280   | 1M KOH      | Adv. Energy Mater. 2018, 8, 1703189   |
| NiFe LDHs nanosheets          | 10         | 300   | 1M KOH      | Nat. Commun. 2014, 5, 44779          |
| CoOOH nanosheets              | 50         | 340   | 1M KOH      | Angew. Chem. Int. Ed. 2015, 54, 8722 |
| NiCo LDHs                     | 50         | 370   | 1M KOH      | Nano Lett. 2015, 15, 1421            |
| Ir-Cu nanoframe structures    | 50         | 340   | 1M KOH      | Chem. Comm. 2016, 52, 3793 – 3796   |
| Ni₃FeAl₀.₉₁-LDHs/NF           | 20         | 304   | 1M KOH      | Nano Energy 2017, 35, 350.           |
| Cu@NCNT/CoₓOᵧ                 | 10         | 370   | 1M KOH      | Adv. Funct. Mater. 2017, 27, 1605717 |
| CoOOH nanosheets              | 50         | 344   | 1M KOH      | Angew. Chem. Int. Ed. 2015, 54, 8722 |
| NiCo LDHs                     | 50         | 430   | 1M KOH      | Nano Lett. 2015, 15, 1421            |

### Table S4 Comparison of the electrocatalytic for overall water splitting of γ-CrOOH/NF to other oxide/hydroxide-based catalysts in 1 M KOH

| Catalyst                      | j (mAcm⁻²) | Potential(V) | Electrolyte | Ref.                                 |
|-------------------------------|------------|--------------|-------------|--------------------------------------|
| γ-CrOOH/NF                    | 10         | 1.56         | 1M KOH      | This work                            |
| CoMnCH                        | 10         | 1.68         | 1M KOH      | J. Am. Chem. Soc.2017,139, 8320      |
| NiFeLDH@NiCoP/NF              | 10         | 1.57         | 1M KOH      | Adv. Funct. Mater. 2018,14, 1706847  |
| Ni₂Fe₁₄O                     | 10         | 1.64         | 1M KOH      | Adv. Energy Mater. 2017, 8, 1701347   |
| NiCo₂S₄                      | 10         | 1.63         | 1M KOH      | Adv Funct Mater. 2016,26 4661-4672   |
| Ni/NiₓMᵧ                     | 10         | 1.61         | 1M KOH      | Adv. Funct. Mater. 2016,26, 3314     |
| Ni₅P₄                         | 10         | 1.70         | 1M KOH      | Angew. Chem. Int. Ed. 2015, 54,     |
|                          |    |    |        |                  |
|--------------------------|----|----|--------|------------------|
| Ni(OH)$_2$/NiSe$_2$      | 10 | 1.78 | 1M KOH | Chem. Mater. 2015, 27, 5702-5711 |
| NiFe-LDH                 | 10 | 1.70 | 1M NaOH| Science 2014, 345, 1593-1596 |
| Co-NC/CNT                | 10 | 1.72 | 1M KOH | J. Mater. Chem. A, 2016, 4, 16057 |

**Reference**

1. Kresse, G.; Joubert, D., From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. *Phys. Rev. B* **1999**, 59, 1758-1775.

2. Perdew, J. P.; Burke, K.; Ernzerhof, M., Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, 77, 3865-3868.

3. Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C., Atoms, Molecules, Solids, and Surfaces-Applications of the Generalized Gradient Approximation for Exchange and Correlation. *Phys. Rev. B* **1992**, 46, 6671-6687.

4. Lebreau, F.; Islam, M. M.; Diawara, B.; Marcus, P., Structural, Magnetic, Electronic, Defect, and Diffusion Properties of Cr$_2$O$_3$: A DFT+U Study. *J. Phys. Chem. C* **2014**, 118, 18133-18145.

5. Rohrbach, A.; Hafner, J.; Kresse, G., Ab Initio Study of the (0001) Surfaces of Hematite and Chromia: Influence of Strong Electronic Correlations. *Phys. Rev. B* **2004**, 70, 125426.

6. Kresse, G.; Furthmüller, J., Efficiency of Ab-Initio Total Energy Calculations for Metals and Semiconductors Using a Plane-Wave Basis Set. *Comput. Mater. Sci.* **1996**, 6, 15-50.