Supporting Information

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

Zemin Sun,^{a,§} Mengwei Yuan, ^{a,§} Han Yang,^a Liu Lin,^a Heyun Jiang,^b Shengsong Ge,^b Huifeng Li,^a Genban Sun,^{a,*} Shulan Ma,^a Xiaojing Yang^a

^aBeijing Key Laboratory of Energy Conversion and Storage Materials, College of Chemistry, Beijing Normal University, Beijing 100875, China

^bCollege of Chemical and Environmental Engineering, Shandong University of Science and Technology, Qingdao 266590, China

§ Zemin Sun and Mengwei Yuan are equally contribution.

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 $(NH_4)_2Cr_2O_7$ 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 N₂H₄·H₂O. 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 γ -CrOOH was measured using inductively coupled plasma mass spectroscopy (ICP-MS, Thermo XSeries II) by dissolving 1 cm * 1cm electrode in 100 mL aquaregia. UV-vis diffuse reflectance spectra were collected on a Shimadzu UV-2450 spectrometer using BaSO₄ as the reference sample. The optical band gaps could be determined by the equation: $E_g = 1240/\lambda_{max}$. Where E_g represents band gap energy, and λ_{max} is the biggest absorption edge of the samples.

Preparation of Cr₂O₃ /NF electrode:

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

Preparation of RuO₂ /NF, IrO₂/NF, Pt/C/NF electrode:

RuO₂ (5 mg) was dispersed in a 1 mL mixed solution (490 μ L water, 15 μ L 5 wt % Nafion solution, and 495 μ L ethanol) and then followed by sonication to obtain catalyst ink. Put the catalyst ink (100 μ L) 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 IrO₂/NF, Pt/C/NF electrode is similar to RuO₂/NF. By weighing the mass difference before and after, the loading of catalysts (RuO₂, IrO₂, Pt/C) was ca. 0.5 mg cm⁻².

Materials characterization:

X-Ray diffraction (XRD) was measured *via* a Phillips X'pert ProMPD diffractometer (CuK α , 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* n a Nicolet-380 FourierTransform infrared spectrometer. X-Ray photoelectron spectra (XPS) were conducted through ESCALAB 250Xi spectrometer (Thermo Fisher) with Al K α 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: $E_{RHE} = E_{Hg/HgO} + 0.098 + 0.0591 * pH$ and the overpotentials (η) for OER is calculated according to the formula: $\eta = E_{RHE} - 1.23$ 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.

Caculation Methods

Based on the spin polarized density functional theory (DFT) and the projector augmented wave

(PAW) method¹ 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).²⁻³ The effective interaction strengths of different 3d orbitals were set as 5.0 for Cr.⁴⁻⁵ A plane-wave basis set⁶ was used with kinetic energy cutoff of E_{cut} =500 eV with a K-point grid of 2×6×3 using the Gamma centered method.



Figure S1 Photographs of (a) amorphous γ-CrOOH and (b) Cr₂O₃.



Figure S2 XRD of catalysts γ -CrOOH /NF and Cr₂O₃/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.

$$E (RHE) - E (HgO/Hg) = 0.098 V + 0.059 * pH (1 M KOH) = 0.926 V (1)$$

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 (RHE) = E (HgO/Hg) + 0.926 V (2)

Figure S9 SEM image of γ -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_2O_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 $Cr_2O_3/NF(a)$ 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_2O_3/NF and γ -CrOOH/NF electrodes. The inset is an enlarged curve of the high-frequency region for Nickel Foam, Cr_2O_3/NF and γ -CrOOH/NF.

Figure S14 UV-visible (UV-vis) diffuse-reflectance spectroscopy (DRS).

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

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

Table S2 Comparison of the electrocatalytic HER activity of γ -CrOOH/NF to otheroxide/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
	50	149	1M KOH	This work
Cr ₂ O ₃ /NF	10	183	1M KOH	This work
	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
MoS ₂ -Ni ₃ S ₂	10	98	1M KOH	ACS Catal. 2017, 7, 2357-2366.
$(Ni_{0.33}Fe_{0.67})_2P$	50	213	1M KOH	Adv. Funct. Mater. 2017, 27 1702513.
			1M KOH	
$NiCo_2S_4$	10	210	1M KOH	Adv Funct Mater. 2016,26 4661-4672
Ni/Ni _x M _y	10	130	1M KOH	Adv. Funct. Mater. 2016,26, 3314

NiCoPS/CC	10	110	1M KOH	Nano Res. 2017, 10, 814-825
NiCo ₂ S ₄ NW/NF	10	210	1M KOH	Adv. Funct. Mater. 2016, 26, 4661
Co-Mo ₂ C	10	118	1M KOH	Adv. Funct. Mater. 26 (2016) 5590
CoO _x @CN	20	134	1M KOH	J. Am. Chem. Soc. 2015, 137, 2688

Table S3 Comparison of the electrocatalytic OER activity of γ -CrOOH/NF to otheroxide/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
Co ₃ O ₄ /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
Ni ₃ FeAl _{0.91} -LDHs/NF	20	304	1M KOH	Nano Energy 2017, 35, 350.
Cu@NCNT/Co _x O _y	10	370	1M KOH	Adv. Funct. Mater. 2017, 27, 1605717
CoOOH nanosheets	50	344	1 M KOH	Angew. Chem. Int. Ed. 2015, 54, 8722
NiCo LDHs	50	430	1 M 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
Ni ₂ Fe _{1-x} O	10	1.64	1M KOH	Adv. Energy Mater. 2017, 8, 1701347
NiCo ₂ S ₄	10	1.63	1M KOH	Adv Funct Mater. 2016,26 4661-4672
Ni/Ni _x M _y	10	1.61	1M KOH	Adv. Funct. Mater. 2016,26, 3314
Ni ₅ P ₄	10	1.70	1M KOH	Angew. Chem. Int. Ed. 2015, 54,

				12361
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

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