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Highly active hollow mesoporous NiFeCr hydroxide as an electrode material for the oxygen evolution reaction and a redox capacitor

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Materials

Glycerol (C₃H₈O₃), ethylene glycol (C₂H₆O₂), ammonium fluoride (NH₄F), NiSO₄·7H₂O, FeSO₄·7H₂O, ZnSO₄·7H₂O, H₂SO₄, boracic acid, CrO₃, and potassium hydroxide (KOH) were obtained from Shanghai Aladdin Bio-Chem Technology Co., Ltd, and all of them are analytical-grade reagents. All electrolyte solutions were prepared using ultrapure water (18.2 M Ω). The nickel foam (NF) (20 mm×10 mm×2 mm) was ultrasonically cleaned with alcohol, acetone, trichloroethylene, hydrochloric acid (5 M), and ultrapure water, successively.

Preparation of HMS-NiFeCrO/NF

The preparation of HMS-NiFeCrO/NF was illustrated in Fig. S1. The electrodeposition was performed at an electrochemical workstation (Model CS310, Wuhan CorrTest Instruments Corp., Ltd., Wuhan, China) in an electrolyte (100 mL) containing 18 g of NiSO4.7H2O, 2 g of FeSO4·7H2O, H2SO4, boracic acid, and 20 g of CrO3. NF was used as a working electrode, titanium mesh-plated platinum as the counter electrode, and a commercial Ag/AgCl (saturated KCl) as a reference electrode (INESA Scientific Instrument Co., Ltd., Shanghai, China). After 10 min at a current density of -30 mA cm⁻², the Ni/Fe/Cr alloy film was coated on NF. Then, dealloying corrosion was conducted by immersing the ternary alloy layer into 1 M HNO₃ solution at room temperature for 1 h to remove iron partially and obtain porous structures. After washed with ultrapure water, the sample was transferred to a vacuum oven at 60 °C and kept for 3 h. Then, the sample was anodized in an electrolyte containing 15 mL glycerol, 15 mL ethylene glycol, 1 mol L⁻¹ ammonium fluoride, and 70 mL ultrapure water at 3 V for 30 minutes. The anodized step has turned the plating metal elemental into oxides and created a much porous structure on the surface. After anodization, the sample was activated by potentiostatic polarization at 1 V (vs Ag/AgCl) in 1 mol L⁻¹ KOH solution for 20 minutes. During the activated process the metal oxides were gradually converted into hydroxides. The final product was dried in the vacuum oven at 60 °C for 3 h, denoted as HMS-NiFeCrO/NF.

Control samples with dealloying treatment (HMS-NiFeZnCrO/NF, HMS-NiZnCrO/NF) using Zn as the sacrificial template (initial 4 g of $ZnSO_4 \cdot 7H_2O$) or without dealloying treatment (NiCrO/NF, NiFeCrO/NF, and NiZnCrO/NF) were prepared in a similar procedure. For comparison, the Ni(OH)₂/NF sample was also synthesized from the electrolyte of NiSO₄·7H₂O.



Fig. S1 Preparation and characterization of HMS-NiFeCrO/NF.

Characterization

The morphologies of the obtained HMS-NiFeCrO/NF was investigated using scanning electron microscopy (SEM) with EDS (EDAS NOVA NANOSEM 450), transmission electron microscopy (TEM) (Tecnai G2 F20 S-TWIN), and X-ray photoelectron spectroscopy (XPS) (ESCALAB 250Xi, Thermo Fisher). The porosity and Brunauer-Emmett-Teller (BET) specific surface was studied by JW-BK222 (JWGB SCI. & TECH. Co. etl). The phase and crystallinity were examined using an X-ray diffraction (XRD) diffractometer (Bruker D8 ADVANCE A25X). The Raman spectrum was recorded using JSM-7610F (JEOL Ltd.). The desorption of water was examined by thermogravimetric analysis (TGA) and effluent gas analysis using a thermogravimetry instrument (Sta449 F5) connected to a mass spectrometer (QMS 403D), manipulated from 150 °C to 800 °C before drying treatment (vacuum drying at 150 °C for 1 h). The ICP-OES (Optima 8000, PerkinElmer, USA) was used to determine the content of iron in the HMS-NiFeCrO/NF.

Electrochemical measurements

Electrocatalytic performances for OER were tested in the O₂-saturated KOH solution. Linear scan voltammogram (LSV) and polarization were performed in a standard three-electrode

electrochemical cell, using an electrochemical station (Model CS310, Wuhan CorrTest Instruments Corp., Ltd.). The prepared electrode was used as a working electrode, Ag/AgCl (saturated KCl) as the reference electrode, and titanium mesh-plated platinum as the counter electrode. Electrochemical impedance spectroscopy (EIS) measurements were carried out in a frequency range from 0.01 Hz to 100 kHz with an amplitude of 10 mV at open circuit potential in 0.1, 1, and 2 mol L⁻¹ KOH aqueous solutions, respectively. The potentials obtained in this study were calibrated relative to the reversible hydrogen electrode (RHE) scale, according to the Nernst equation ($E_{RHE} = E_{Ag/AgCl} + 0.197 V + 0.059 \times pH$).

Pseudocapacitive performances of the HMS-NiFeCrO/NF material were characterized in a standard three-electrode system using an electrochemical workstation (Model CS310, Wuhan CorrTest Instruments Corp., Ltd.). The counter electrode was platinum-plated titanium mesh, the reference electrode was a commercial Ag/AgCl (saturated KCl), and the working electrode was HMS-NiFeCrO/NF. A series of electrochemical tests were conducted on the workstation, including cyclic voltammetry (CV) and galvanostatic charge/discharge. Besides, the stabilities of the electrodes were also evaluated using a scan rate of 100 mV s⁻¹. For practical application purposes, an asymmetric supercapacitor was assembled using the HMS-NiFeCrO/NF as the positive electrode, activated carbon (AC/NF) as the negative electrode, and KOH (2 mol L⁻¹) as the electrolyte. The AC/NF electrode was prepared by adding 76 wt % AC, 10 wt % carbon black, 10 wt % polytetrafluoroethylene, and 4 wt % sodium carboxymethylcellulose into 20 wt % water, and the resulting mixture was pressed onto an NF substrate (current collector). Finally, the electrode was dried at 65 °C for 12 h. Energy (*E*) and power (*P*) densities were calculated based

on specific capacity by using the following equations: $E = \frac{1}{7.2}CV^2 Wh kg^{-1}$, $P = \frac{3600E}{t} W kg^{-1}$, where *C* is the specific capacitance of the full cell, and *V* and *t* are the operating voltage and the discharge time, respectively.

DFT calculations

Density functional theory (DFT) calculations were performed using the Cambridge Sequential Total Energy Package (CASTEP).¹ Electron-ion interactions were modeled by projector augmented wave (PAW) potentials.² Exchange and correlation effects for structural relaxation were approximated by generalized gradient approximation (GGA) using the PerdewBurke-Ernzerhof (PBE) functional.^{2, 3} The Coulomb and exchange interactions in the pristine β -Ni(OH)₂ and NiFeCrO systems were described by setting the effective on-site Coulomb and exchange parameters U-J to be 2.8 eV, 3.2 and 2.5 eV for Ni, Fe and Cr, respectively. The cut-off energy was set at 400 eV for the plane-wave basis in all calculations. K-points were sampled under the Monkhorst-Pack scheme for Brillouin-zone integration.⁴ The corresponding NiFeCrO (110) surface model is shown in Fig. S12b, where the atomic ratio of Ni:Cr:Fe:O was approximately set to 1.3:1:0.04:1.18. The atomic structures for all models were relaxed with self-consistency accuracy of 10⁻⁴ eV for electronic loops until the forces on all atoms were < 0.02 eV/Å.



Fig. S2 (a) LSV curves of the NiFeCrO/NF, NiCrO/NF, and treated NF with the same process as etching, oxidation, and activation tested at 2 mV s⁻¹ in 1 M KOH without *iR* compensation. (b) Corresponding Tafel plot of (a). (c) CV curves of NiCrO/NF and NiFeCrO/NF samples in 2 mol L⁻¹ KOH at 5 mV s⁻¹.

The OER and capacitive properties testing of NiFeCrO/NF and NiCrO/NF electrodes were performed in 1 M KOH solution (Fig. S2). Moreover, the OER performances of these samples were also evaluated by the Tafel slope according to the equation $\eta = a + b \lg j$, where *a* is the overpotential that the current density equal to 1 A cm⁻², *b* is the Tafel slope, and *j* is the current density. The LSV curve and slope of the Tafel curve demonstrated that the incorporation of Fe enhanced the OER significantly (Fig. S2a,b). As for capacitive properties, the specific capacity calculated by integration of the CV curve of NiFeCrO/NF and NiCrO/NF (Fig. S2c) was 562 and 1013 F g⁻¹, respectively.



Fig. S3 (a) CV curves of HMS-NiZnCrO/NF with different dealloying times in 2 mol L⁻¹ KOH at 5 mV s⁻¹. (b) CV curves of HMS-NiFeZnCrO/NF (30 min dealloying time for NiFeZnCrO/NF), HMS-NiZnCrO/NF (30 min dealloying time for NiZnCrO/NF), and NiFeCrO/NF samples. (c) LSV curves of HMS-NiFeZnCrO/NF, HMS-NiZnCrO/NF, and NiFeCrO/NF samples at 2 mV s⁻¹ in 1 M KOH without iR compensation. (d) Corresponding Tafel plot of (c).

When Zn was used as the sacrificial template for the preparation of HMS-NiZnCrO/NF, different dealloying times (5, 10, 20, 30, 40, and 60 min) were treated for the optimal condition. As Fig. S3a shown, the CV curves' integral areas were increased with the dealloying time, and at 30 min the integral area reached the maximum. Then the 30 min was determined as the suitable dealloying time for the Zn system. Under such a condition, the specific capacity was determined as 1300 F g⁻¹. Comparison of the CV curves of NiFeCrO/NF with HMS-NiFeZnCrO/NF and HMS-NiZnCrO/NF (Fig. S3b) revealed that the HMS, as well as Fe dopant, improved the capacity.⁵ As for OER properties (Fig. S3c), the LSV curves of HMS-NiFeZnCrO/NF showed the faster growth of current density than that of HMS-NiZnCrO/NF. As for the Tafel slope analysis (Fig. S3d), HMS-NiFeZnCrO/NF also gave a smaller slope.



Fig. S4 (a) CV curves of HMS-NiFeZnCrO/NF samples with different initial addition of $FeSO_4 \cdot 7H_2O$ in the electrolytes and 30 min dealloying (5 mV s⁻¹ in 2 mol L⁻¹ KOH). (b) The specific capacity of these samples in (a)

Starting from the HMS-NiFeZnCrO/NF system, a series of samples containing different initial amounts of $FeSO_4 \cdot 7H_2O$ (0.5, 1, 2, 4, 8, and 12 g) were prepared by electroplating the nickel/zinc/iron/chromium quaternary alloy layer on the NF, with electrolytes containing 18 g of NiSO₄·7H₂O, 4 g ZnSO₄·7H₂O, 2 g of H₂SO₄, 4 g of boracic acid and 20 g of CrO₃ and FeSO₄·7H₂O, followed by dealloying, oxidation, and activation. The results (Fig. S4) showed that the specific capacity of the as-prepared electrodes with 1 g initial addition of FeSO₄·7H₂O gave the maximum (1558 F g⁻¹).



Fig. S5 (a) CV curves of HMS-NiFeCrO/NF samples with different dealloying times (5 mV s⁻¹ in 2 mol L⁻¹ KOH). (b) LSV curves of these samples without *iR* compensation (2 mV s⁻¹ in 1 mol L⁻¹ KOH).

When using Fe as the sacrificial template, the HMS-NiFeCrO/NF sample was prepared by electroplating the nickel/iron/chromium ternary alloy layer on the NF (using 18 g NiSO₄·7H₂O, 2 g H₂SO₄, 4 g boracic acid, 20 g CrO₃, and 1 g FeSO₄·7H₂O), followed by dealloying, oxidation, and activation, as addressed before in the preparation section.

The dealloying times (0, 30, 60, 80, 100, and 120 min) tests (Fig. S5a) showed that the 100 min dealloying time corresponded to the largest integral area. Those samples obtained at 120, 80 and 60 min led to the values relatively lower but very close to that of 100 min. As for the OER property (Fig. S5b), the anodic current density of a 60 min dealloying sample increased fastest. To combine these two aspects, the 60 min of dealloying time was chosen as the operational condition, where the initial Fe played bifunctional roles of both sacrificial template and indispensable dopant.



Fig. S6 Electrochemical measured of these HMS-NiFeCrO/NF samples synthesized by electroplating in electrolytes containing different amounts of precursor $FeSO_4 \cdot 7H_2O$ (1, 2, 4, 8, 12 and 20 g) with 60 min dealloying time. (a) CV curves of these samples in 2 M KOH at 5 mV s⁻¹. (b) The specific capacity of these electrodes versus the current density of (a). (c) LSV curves of these electrodes tested at 2 mV s⁻¹ in 1 M KOH without *iR* compensation. (d) The overpotentials of these electrodes tested in 50 mA cm⁻². (e) Corresponding Tafel plot of (c). (f) Nyquist plots of these electrodes obtained in 2 M KOH aqueous solution. Inset of (e) was the equivalent circuit.

The effects of the initial content of Fe were studied by electroplating the nickel/iron/chromium ternary alloy layer on the NF (18 g NiSO₄·7H₂O, 2 g H₂SO₄, 4 g boracic acid, 20 g CrO₃, and a series of initial amounts of FeSO₄·7H₂O, 1, 2, 4, 8, 12 and 20 g FeSO₄·7H₂O), followed by dealloying, oxidation, and activation.

The 2 g $FeSO_4 \cdot 7H_2O$ sample achieved the biggest integral area (Fig. S6a) as well as the highest specific capacitance (Fig. S6b, 1960 F g⁻¹). Although the 2 g $FeSO_4 \cdot 7H_2O$ precursor

sample did not has the lowest overpotential at a current density of 50 mA cm⁻² (the second-lowest, 294 mV) (Fig. S6c,d), its Tafel slope was the lowest (83 mV dec⁻¹) among them (Fig. S6e), indicating fast electron and mass transfer between the catalyst and the electrolyte.^{6, 7} Nyquist plots testing (Fig. S6f) suggested that the 2 g FeSO₄·7H₂O sample exhibited the smallest equivalent series resistance (R_s) and charge transfer resistance (R_{ct}) values (Table S1), revealing the low intrinsic resistance and high reactivity with electrolyte.

HMS-NiFeCrO/NF (with different FeSO4·7H2O	$R_{s}\left(\Omega ight)$	$R_{ct}(\Omega)$	
precursor)			
0 g	3.12	2300	
1 g	2.11	12.79	
2 g	1.95	2.82	
4 g	2.29	5.63	
6 g	2.17	8.98	
8 g	1.92	7.13	
12 g	2.36	5.61	
20 g	2.13	11.84	

Table S1 Electrochemical parameters obtained from EIS in 2 mol L⁻¹ KOH solutions

The above results demonstrated that the 2 g $FeSO_4 \cdot 7H_2O$ precursor in 100 mL aqueous electrolyte, usage of Fe as the sacrificial template, and 60 min dealloying time were the optimal conditions for the preparation of HMS-NiFeCrO/NF. These advantages would enable HMS-NiFeCrO/NF to have better coulomb efficiency and reversibility.⁸

In order to determine the content of iron accurately in the HMS-NiFeCrO/NF obtained under the optimal condition, ICP-OES (Optima 8000, PerkinElmer, USA) was used. The content of Fe in the coating of HMS-NiFeCrO/NF was found to be 2.7 wt %. The ICP and single-factor experiments of initial content of $FeSO_4 \cdot 7H_2O$ demonstrated that a small amount of Fe was conducive to the decrease of internal resistance and improvement of electrochemical performance of the HMS-NiFeCrO/NF electrode.



Fig. S7 HRTEM images of HMS-NiFeCrO to show the possible mesopores in relatively lighter (low

contrast) zones highlighted using dotted lines.



Fig. S8 (a) XRD analysis of HMS-NiFeCrO and pure Ni(OH)₂. (b) Desorption of water from HMS-NiFeCrO measured by mass spectrometry (M = 18) at temperatures from 150 to 800 °C. (c) Raman spectra of HMS-NiFeCrO and pure Ni(OH)₂.

To investigate the crystallinity, the HMS-NiFeCrO active layer was ultrasonically scraped from the NF substrate. And the Ni(OH)₂/NF was synthesized from the electrolyte only containing NiSO₄·7H₂O and the active Ni(OH)₂ layer was also ultrasonically scraped for characterization. As shown in Fig. S8a, the pure Ni(OH)₂ sample corresponds to β -Ni(OH)₂ (JCPDS Card No. 14-0117) which was similar to the XRD pattern reported in references.^{9, 10} And the HMS-NiFeCrO curve shows three peaks centered at 18.5°, 36.1°, and 61.5°, respectively. These three peaks can be ascribed to one phase, which is very similar to the pattern for β -Ni(OH)₂ (JCPDS Card No. 14-0117).^{9, 10} Then, the unit cell parameters were determined as a hexagonal lattice using Jade 6.5 software. The three diffraction peaks could be indexed well to (001), (101) and (111) planes of hexagonal phase structure.^{9, 10} The hexagonal β -Ni(OH)₂ was a layered structure, in which each layer of Ni atoms consists of two sheets of hydroxyls in hexagonal close packing and the neighbor layers that are parallel to the basal plane (001) are weakly stacked by van der Waals forces with an interlayer distance (*d*) of 0.46 nm.^{9, 10} As for the as-prepared HMS-NiFeCrO, the calculated *d* for the plane (001) was 0.49 nm, which is larger than the pure β -Ni(OH)₂ (0.46 nm). This may be due to the incorporation of Cr and Fe. The calculated unit cell parameters of HMS-NiFeCrO are *a* = 3.14 Å, *b* = 3.14 Å, *c* = 4.628 Å (α = 90°, β = 90°, γ = 120°).

The presence and decomposition of Ni(OH)₂ were further proved by the thermogravimetrymass spectrometry (TG-MS) analysis. Fig. S8b showed the characteristic peak (264 °C) and the corresponding desorbed material was detected with the molecular mass of 18. It was reported that weight loss around 260 °C is the typical thermal decomposition temperature of Ni(OH)₂ for the Ni(OH)₂ \rightarrow NiO + H₂O reaction.¹¹ Because there was a drying treatment (vacuum drying at 150 °C for 1 h) before the TG-MS measurement, the as-detected desorbed material (molecular mass of 18) should be H₂O, generated by the decomposition of Ni(OH)₂ at 264 °C.

In the Raman spectrum of the Ni(OH)₂ sample (Fig. S8c), the signals at \sim 300 cm⁻¹ and 443 cm⁻¹ could be contributed by Ni(OH)₂. Similar observations were found in related works.¹²⁻¹⁴ For the HMS-NiFeCrO sample the signal around 450 cm⁻¹ could be due to the Ni(OH)₂ while the peak at 534 cm⁻¹ may be ascribed to Cr₂O₃, according to to the reference reports. ^{15, 16}



Fig. S9 Nitrogen adsorption-desorption isotherm (a) and corresponding Barrett-Joyner-Halenda (BJH) pore size distribution (b) of HMS-NiFeCrO and NF substrate, respectively.



Fig. S10 EDS point analysis of HMS-NiFeCrO (a) and elemental mapping of Ni (b), Cr (c), Fe (d) and O (e). The scale bar was 0.5 μ m.



Fig. S11 (a) Nyquist plots of the HMS-NiFeCrO/NF electrode obtained in 0.1, 1, and 2 M KOH aqueous solution. (b) The Tafel plot corresponding to Fig. 4a. (c) Chronoamperometry curves in 1 and 0.1 M KOH with the constant potential of 1.62 and 1.6 V (vs RHE), respectively. (d) The equivalent circuit diagram for Fig. S11a.



Fig. S12 Atomic structures of (a) β -Ni(OH)₂ unit cell and (b) NiFeCrO (110) surface model. The (1~4) demonstrated the four steps for the free energy of the two materials.

The β -Ni(OH)₂ unit cell with calculated lattice constants of a = 3.15 Å, b = 3.17 Å and c = 4.61 Å ($\alpha = 90^{\circ}$, $\beta = 90^{\circ}$, $\gamma = 120^{\circ}$) was assembled into a 2×2 supercell as shown in Fig. S12a.^{17, 18} A vacuum slab of 10 Å in thickness was applied to prevent interaction between two neighboring surfaces. Five top-most atomic layers were relaxed to optimize the surface structure and all other atoms were frozen to simulate bulk structure. The corresponding NiFeCrO (110) surface model is shown in Fig. S12b where substitutional Fe and Cr dopants are considered. NiFeCrO unit cell with calculated lattice constants of a = 3.16 Å, b = 3.173 Å, and c = 4.63 Å and was assembled into a 2×2 supercell as shown in Fig. S12b.

The free energy was calculated using Eq. S1^{19, 20}:

$$G = E + ZPE - TS \tag{Eq. S1}$$

Where, *G*, *E*, *ZPE*, and *TS* were the free energy, total energy from DFT calculations, zero-point energy, and entropic contributions (*T* was set to be 298K), respectively.²⁰ *ZPE* could be derived after frequency calculation by Eq. S2:

$$ZPE = \frac{1}{2} \sum hv_i$$
 (Eq. S2)

TS values of H_2O and H_2 were from previous reports.^{1, 20, 21} And the *TS* values of adsorbed species were calculated after obtaining the vibrational frequencies (Eq. S3):

$$TS_{\nu} = k_{B}T \left[\sum_{K} \ln(\frac{1}{1 - e^{-h\nu/k_{B}T}}) + \sum_{K} \frac{h\nu}{k_{B}T} \frac{1}{(e^{h\nu/k_{B}T} - 1)} + 1 \right]$$
(Eq. S3)

According to the previous study on the OER pathway in alkaline media,²¹ the OER pathway was described as the adsorption of successive intermediate species on the catalyst and the relevant reaction energies were as follows (Eq. S4 \sim Eq. S7):

$$OH^- + cat \rightarrow OH\text{-}cat + e^-$$
 (Eq. S4)

$$\cdot OH\text{-}cat + OH\text{-} \rightarrow \cdot O\text{-}cat + H_2O + e^{-1}$$
(Eq. S5)

$$O\text{-}cat + OH^{-} \rightarrow OOH\text{-}cat + e^{-}$$
(Eq. S6)

$$\cdot OOH\text{-}cat + OH^{-} \rightarrow O_2 \uparrow + H_2O + e^{-}$$
(Eq. S7)

The *cat* represented the active site when OER occurred. The $\cdot OH$, $\cdot O$, $\cdot OOH$ represented the intermediate species adsorbed on the active sites. In order to evaluate OER activity, we calculated the free energy ($\Delta G_1 \sim \Delta G_4$) using the computational standard hydrogen electrode model. The free energy calculation could be obtained as follows:

$$\Delta G_1 = G_{OH - cat} - G_{cat} - G_{H_20} + \frac{1}{2}G_{H_2} - eU + K_B ln 10 \cdot pH$$
(Eq. S8)

$$\Delta G_2 = G_{0 - cat} - G_{0H - cat} + \frac{1}{2}G_{H_2} - eU + K_B ln 10 \cdot pH$$
(Eq. S9)

$$\Delta G_3 = G_{00H - cat} - G_{0 - cat} - G_{H_20} + \frac{1}{2}G_{H_2} - eU + K_B ln 10 \cdot pH$$
(Eq. S10)

$$\Delta G_4 = 4.92 - \Delta G_1 - \Delta G_2 - \Delta G_3 \tag{Eq. S11}$$

It should be noted that -eU represented the free energy changes for one-electron transfer where U was electrode potential represented the standard hydrogen electrode. For pH \neq 0, pH affected on free energy could be defined as $-K_BT \cdot \ln 10 \cdot pH$, where K_B was Boltzman constant. ΔG_4 was calculated by $4.92 \cdot \Delta G_1 \cdot \Delta G_2 \cdot \Delta G_3$ to avoid calculating the O₂ adsorption and desorption. It was known that the DFT calculation might not accurately describe the free energy of the O₂ molecule in the gas phase and hence we used H₂O and H₂ as a reference and from there we extracted the free energy of O₂ through the reaction O₂ + 4(H⁺ + e⁻) \rightarrow 2H₂O. The equilibrium potential for this reaction was 1.23 V and since it was a four-electron transfer reaction, the full energy was 4 × 1.23 = 4.92 eV. This analysis was based on the scheme developed by Norskov's group.²² The overpotential of OER in this mechanism was defined as $\eta_{OER} = max(\Delta G_{OER}/e) - 1.23 V$.²¹

Thus, pristine and Cr, Fe doped β -Ni(OH)₂ surface models (Fig. S12) are created to examine the effect of dopants. Fig. 4b elucidates the free energy diagrams of typical OER processes involving four elementary steps (HO·, ·O, ·OOH, and O₂), where the one with the highest free energy change ΔG is the potential limiting step (PLS).¹ The PLS for β -Ni(OH)₂ is determined to be the deprotonation step (HO· \rightarrow O· + H⁺ + e⁻) having a ΔG_2 value of 2.2 eV and a corresponding calculated overpotential η of 0.97 V. Interestingly, the PLS for NiFeCrO is determined to be the deprotonation step (H₂O(*l*) \rightarrow HO· + H⁺ + e⁻) having a ΔG_1 value of 1.91 eV and a corresponding calculated overpotential η of 0.68 V, revealing the origin of the enhanced OER activity.



Fig. S13 Electrochemical measurements in 2 mol L⁻¹ KOH. (a) CV curves of HMS-NiFeCrO/NF, NF, and treated NF obtained using the same process experiencing the etching, oxidation, and activation. (b) CV curves of HMS-NiFeCrO/NF at different scan rates ranging from 5 to 100 mV s⁻¹. (c) Specific capacity as a function of the scan rate. (d) and (e): Cycling stability measured through CV at 100 mV s⁻¹ for HMS-NiFeCrO/NF.

As shown in Fig. S13a, the integral area CV curve of HMS-NiFeCrO/NF was the biggest indicating the optimal capacitance performance. The CV curves of the HMS-NiFeCrO/NF electrode measured at different scan rates were shown in Fig. S13b. The faradaic reactions caused redox peaks were present in CV plots, indicating the pseudocapacitive characteristics of the HMS-NiFeCrO/NF.^{23, 24} And the HMS-

NiFeCrO/NF electrode showed obvious redox couple peaks that can be represented by the following electrochemical reaction:¹⁰

$$\beta - Ni(OH)_2 + OH^- \leftrightarrow \beta - NiOOH + H_2O + e^-$$
(Eq. S12)

For HMS-NiFeCrO/NF, the increased layer spacing (0.49 nm) would bind more hydroxyls and other ions.¹⁰ These structurally bonded hydroxyls and other ions provide the passage for proton diffusion between layers, which may accelerate the proton diffusion rate and improve the capacity.²⁵ The reason can be ascribed to the hierarchical porous structures that provide a high specific surface area to improve electron transport, enhance rapid ion transport, and mitigate diffusion limitations throughout the entire HMS-NiFeCrO/NF.²⁶ From an elemental point of view, the incorporated Cr^{3+} and Fe^{3+} into β -Ni(OH)₂ would present a special electronic configuration, which facilitates charge transfer and electron capture thus to increase the conductivity and capacity.²⁷



Fig. S14 Ragone plot related to the energy and power densities of HMS-NiFeCrO/NF//AC/NF asymmetric supercapacitor. Inset: a photograph of the blue LED powered by two supercapacitors in series.



Fig. S15 The capacitive contributions to the total charge storage. Voltammetric responses for HMS-NiFeCrO/NF at scan rates of 0.5 (a), 1 (b), 2 (c) and 5 (d) mV s⁻¹. The capacitive and diffusion controlled contribution at different scan rates (e).

The energy storage mechanism of the pseudocapacitive HMS-NiFeCrO/NF was investigated by separating the total charges into capacitive and diffusion controlled components,^{28, 29} as described by K_1v (capacitive) and $K_2v^{1/2}$ (diffusion-controlled) contributions using $i(V) = K_1v + K_2v^{1/2}$, where *i* is the current at a fixed potential (V) and *v* is the sweep rate. Fig. S15 (a-d) showed a typical separation of capacitive and diffusion currents at scan rates of 0.5, 1, 2, and 5 mV s⁻¹. As shown in Fig. S15e, the capacitive controlled process contributed to 57.3%, 62.7%, 71.5%, and 82.6% of the total charge

storage at 0.5, 1, 2, and 5 mV s⁻¹, respectively. This indicated that the dominant charge storage was the capacitive mechanism, endowing it with high charge storage kinetics and cycling stability.²⁸



Fig. S16 Total density of states of β -Ni(OH)₂ and NiFeCrO (a). Partial density of states (PDOS) for Cr (b), PDOS for Fe (c), PDOS for Ni (d), PDOS for O (e). The absorption energy for OH⁻ (f).

The density of states (DOS) has been derived from giving a deep insight into the orbital interactions of NiFeCrO towards the enhanced capacitance property. Fig. S16a displays the total density of states (TDOS) for β -Ni(OH)₂ and NiFeCrO. They showed similar TDOS patterns. The peaks around -20.0 eV are the σ -bondings while states near Fermi level are contributed by valence orbitals. For NiFeCrO, a smaller bandgap at the Fermi level than β -Ni(OH)₂ was observed, demonstrating the enhanced electrical conductivity. The increased DOS at the Fermi level of NiFeCrO is mainly because Cr and Fe heteroatom metallizes the relaxed structure of β -Ni(OH)₂. The Cr shows most electronic

states near the Fermi level which demonstrated it plays a greater role in improving the electrical conductivity of NiFeCrO (Fig. S16b).³⁰ The DOS of Fe shows more states from -5.0 eV to the Fermi level, which indicates a more negative d-band center and easier adsorption of OH⁻ (Fig. S16c). This has been demonstrated by the absorbed energy of the NiFeCrO for OH- (Fig. S16f). The DOS of Ni has been influenced by the doped Cr and Fe that make the Ni shows more charge density near the Fermi level, which provides more charge carriers for the redox reaction (Fig. S16d).³⁰ At the same time, DOS of O shifts more negative to the Fermi level, indicating enhancement adsorption of OH- due to the influence of Cr and Fe (Fig. S16e). In summary, the outstanding electronic conductivity and better oxidation in the NiFeCrO system are the direct influence on the enhanced driving force for the electrochemical properties and the charge/discharge process. The results demonstrated that Cr plays a greater role in improving the electrical conductivity of NiFeCrO, and Fe is beneficial for improving the adsorptive properties of OH⁻. The enhanced total density of states at the Fermi level for NiFeCrO indicates that the synergistic interaction of Ni, Fe, and Cr at the surface contributes more free electrons and more active surfaces for the redox reaction.

HMS- NiFeCrO/NF	$R_{s}\left(\Omega ight)$	$\mathbf{R}_{\mathrm{ct}}\left(\Omega ight)$
1 M KOH	2.28	9.12
0.1 M KOH	2.47	47.31
2 M KOH	1.95	2.82

 $Table \ S2 \ {\sf Electrochemical parameters obtained from EIS in KOH solutions}$

 $\label{eq:Table S3} Table S3 Comparison of the OER performances of HMS-NiFeCrO/NF electrode and some other Ni-based electrodes at 10 mA cm^{-2} in 1 M KOH$

Electrode	Overpotential (mV)	Reference
NiFeCr-6:2:1@CP	225	31
NiFe-MOF-74	223	32
N,S-rGO/WSe ₂ /NiFe-LDH	250	33
NiCr-LDH	364(100 mA cm ⁻²)	27
NiGa LDH	450	34
NiFe@CA/CC	269	35
NiFeCr-LDHs/g-C ₃ N ₄	223	36
Ir-doped NiCo LDH	220	37
H-3DRG@NiCo-LDH	264	38
HMS-NiFeCrO/NF	210	Present work

Electrode	Current density or scan rate (A g ⁻¹)	Specific capacitance (F g ⁻¹)	Stability	Reference
Ni _x S _y /rGO	20	581 C g ⁻¹	5000/80% enhanced	39
(Fe,Cr) ₂ O ₃	5 mV s^{-1}	16.88 mF cm ⁻²	10000/90%	40
N,S-rGO/WSe ₂ /NiFe-LDH	1	1184	2000/92.3%	33
NiCoFe-NC	12	1050	5000/92.2%	41
NiO-CNT	2 (mV s ⁻¹)	878.19	4000/89%	42
NiFe@CA/CC	2	861	5000/96%	35
NiS	1	874.5	3000/90.2%	43
0.1Cu-Ni ₃ S ₂	1	847	5000/94.0%	44
HMS-NiFeCrO/NF	2	1538	10000/0.5% enhanced	Present work

 Table S4 Comparison of the supercapacitive performances of HMS-NiFeCrO/NF electrode

 and some other Ni-based electrodes

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