Electronic Supplementary Information

Engineering Borate Modified NiFe Layer Double Hydroxides Nanoarrays as “Hydroxyl Ions Hungry” Electrocatalysts for Enhanced Oxygen Evolution

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Experimental methods

Materials:

Nickel nitrate hexahydrate (Ni(NO$_3$)$_2$.6H$_2$O, Beijing Chemical Reagent Co., Ltd.), iron nitrate nonahydrate (Fe(NO$_3$)$_3$.9H$_2$O, Beijing Chemical Reagent Co., Ltd.), Cobaltous Nitrate hexahydrate (Co(NO$_3$)$_2$.6H$_2$O, Beijing Chemical Reagent Co., Ltd.), Aluminum nitrate nonahydrate (Al(NO$_3$)$_3$.9H$_2$O, Beijing Chemical Reagent Co., Ltd.), ammonium fluoride (NH$_4$F, Shanghai Macklin Biochemical Co.), urea (CH$_4$N$_2$O, Beijing Chemical Reagent Co., Ltd.), nitric acid (HNO$_3$, Beijing Chemical Reagent Co., Ltd.), ethanol (C$_2$H$_5$OH, Beijing Chemical Reagent Co., Ltd.), potassium tetraborate tetrahydrate (K$_2$B$_4$O$_7$.4H$_2$O, Sigma-Aldrich Chemical Reagent Co., Ltd.) potassium hydroxide (KOH, Beijing Chemical Reagent Co., Ltd.), Nafion solution (Sigma-Aldrich Chemical Reagent Co. Ltd.), RuO$_2$ (Shanghai Macklin Biochemical Co. Ltd.). All the materials in this experiment were used directly without any purification.

Preparation of NiFe-LDHs /CP electrode:

The NiFe-LDHs/CP electrode was prepared via a facile hydrothermal method. 0.30 mmol Ni(NO$_3$)$_2$.6H$_2$O, 0.10 mmol Fe(NO$_3$)$_3$.9H$_2$O, 6 mmol NH$_4$F, 10 mmol urea and the carbon paper were dissolved into deionized water (80 mL) to ultrasonic treatment for 30 min. The carbon paper was pretreated in HNO$_3$ and then cleaned via sonication in deionized water and ethanol. Then, the mixture was transferred into a 100 ml Teflon-lined stainless steel autoclave to maintain at 120 °C for 12 h. After it was cooled to room temperature, the electrode was ultrasonicated with water and ethanol several times and then dried at 80 °C.

Preparation of BA-NiFe-LDHs /CP electrode:

The BA-NiFe-LDHs/CP electrode was prepared via second hydrothermal method procedure. The
as-prepared NiFe-LDHs/CP was put into 80 mL saturated potassium tetraborate tetrahydrate solution and then transferred into 100 mL Teflon-lined stainless steel autoclave to maintain 12 h at 120 °C. After it was cooled to room temperature, the electrode was ultrasonicated with water and ethanol several times and then dried at 80 °C.

**Preparation of CoFe-LDHs/CP, NiCo-LDHs/CP, NiAl-LDHs/CP and CoAl-LDHs/CP electrode:**
All these electrodes were produced *via* a hydrothermal method, which was similar to the “Preparation of NiFe-LDHs /CP electrode”.

**Preparation of BA-CoFe-LDHs/CP, BA-NiCo-LDHs/CP, BA-NiAl-LDHs/CP and BA-CoAl-LDHs/CP electrode:**
All these electrodes were produced *via* second hydrothermal method procedure, which was similar to the “Preparation of BA-NiFe-LDHs /CP electrode”.

**Preparation of RuO$_2$ /CP electrode:**
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 on the surfaces of CP. Finally, the electrode was dried at 80 °C overnight.

**Materials characterization:**
X-Ray diffraction (XRD) was performed on a Phillips X’pert ProMPD diffractometer (CuKα, $\lambda$=1.54056 Å, the generator setting was 40 kV and 40 mA). Field emission scanning electronic microscope (FESEM) images were taken *via* a Hitachi scanning electron microscope with an acceleration voltage of 10 kV. 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, Hg/HgO electrode as the reference electrode, and as-prepared working electrode as the working electrode). The OER 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 (\(\eta\)) 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.

**Computational Methods.**

All the first-principles DFT calculations were performed using Vienna *ab initio* simulation package (VASP).\(^1\) The exchange-correlation interactions were treated with the Pseudowave-Perdew-Burke-Ernzerhof (PBE) functional.\(^2\) The interaction between the ionic cores and the valence electrons were described by the projector-augmented wave (PAW) approach.\(^3\) The van der Waals interactions were considered using the Grimme’s DFT-D3 method.\(^4\) The structure optimization for atomic coordinates was performed with a 2 × 2 × 1 Monkhorst–Pack \(k\)-point mesh.\(^5\) A plane-wave basis set with an energy cutoff of 400 eV was used with a 0.01 eV/Å convergence threshold on each atom for force.

All the adsorption models for BA-NiFe-LDHs and NiFe-LDHs were created and cut alone the (0 0 1) direction. To avoid the interaction between two neighboring images, the vacuum space along the \(z\)
The adsorption energies of OH groups on two substrates were defined as:

\[ E_{ads} = E_{system} - E_{substrate} - E_{OH} \]

where \( E_{system} \) is the DFT calculated energy of the adsorption system, the \( E_{substrate} \) is the energy of the substrate, and \( E_{OH} \) means the energy of OH.

**Figures and Tables**

![Figure S1](image)

*Figure S1* XRD patterns of carbon paper.
Figure S2 XPS images of O 1s region for NiFe-LDHs and BA-NiFe-LDHs respectively.

Figure S3 the FT-IR of BA-NiFe-LDHs and NiFe-LDHs.
Figure S4 SEM of NiCo-LDHs /CP in low magnification

Figure S5 The digital image of electrolytic cell with electrode.
Figure S6 The LSV curves of hydrogen electrode reactions on Pt wire.

Figure S7 The polarization curves of CP, NiFe-LDHs/CP and BA-NiFe-LDHs/CP for the OER in 1.0 M KOH solution (scan rate 5 mV s\(^{-1}\))
Figure S8 the XRD patterns and the polarization curves for the OER in 1.0 M KOH solution (scan rate 5 mV s⁻¹) of CoFe-LDHs/CP and BA-CoFe-LDHs/CP (a), (b); NiCo-LDHs/CP and BA-NiCo-LDHs/CP (c), (d); NiAl-LDHs/CP and BA-NiAl-LDHs/CP (e), (f); CoAl-LDHs/CP and BA-CoAl-LDHs/CP (g), (h); respectively.
**Figure S9** Nyquist plots of BA-NiFe-LDHs/CP and NiFe-LDHs/CP. Inset: an equivalent circuit used for fitting data.

**Figure S10** SEM of BA-NiFe-LDHs/CP after stability test in 1.0 M KOH.
Figure S11 The XRD of the BA-NiFe-LDHs/CP before and after durability tests.

Figure S12 CVs of (a) NiFe-LDHs/CP and (b) BA-NiFe-LDHs/CP in the non-faradaic capacitance current range at scan rates of 20, 40, 60, 80, and 100 mV s\(^{-1}\)
**Figure S13** The capacitive currents at 0.075 V vs. SCE as a function of scan rate for electrodes. 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 S14** the pH value-time curve with NiFe-LDHs and BA-NiFe-LDHs added in the fifth min (the same weight NiFe-LDHs and BA-NiFe-LDHs powder in the same volume of solution (0.1 mg/ml)).
### Table S1: Comparison of OER performance in alkaline for NiFe-LDHs@B$_2$O$_3$/CP with other Ni-based and Co-based OER electrocatalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$j$ (mA cm$^{-2}$)</th>
<th>Mass Loading (mg/cm$^2$)</th>
<th>$\eta$ (mV)</th>
<th>Electrolyte</th>
<th>Ref.</th>
</tr>
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<tbody>
<tr>
<td><strong>BA-NiFe-LDHs/CP</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.21</td>
<td>203</td>
<td>1M KOH</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.21</td>
<td>255</td>
<td>1M KOH</td>
<td>This work</td>
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<tr>
<td></td>
<td>100</td>
<td>0.21</td>
<td>293</td>
<td>1M KOH</td>
<td>This work</td>
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<tr>
<td>NiFe-LDHs/Ni Foam</td>
<td>50</td>
<td>-</td>
<td>336</td>
<td>1M KOH</td>
<td>Science, 2014, 345, 1593–1596</td>
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<tr>
<td>NiFeCr LDHs/GC</td>
<td>10</td>
<td>0.20</td>
<td>280</td>
<td>1M KOH</td>
<td>Adv. Energy Mater. 2018, 8, 1703189</td>
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<td>CoFe2O4/PANIM WCNTs</td>
<td>10</td>
<td>0.28</td>
<td>314</td>
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<td>J. Mater. Chem. A, 2016, 4, 4472-4478.</td>
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<td>CoFeMo (oxy)hydroxides/GC</td>
<td>10</td>
<td>0.20</td>
<td>277</td>
<td>1M KOH</td>
<td>Chem. Sci. 2017, 8, 3484</td>
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<tr>
<td>FeOOH/NiFe LDHs@CCH NAs-NF</td>
<td>10</td>
<td>-</td>
<td>220</td>
<td>1M KOH</td>
<td>J. Mater. Chem. A, 2018, 6, 3397</td>
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<tr>
<td>NiFe LDH@CNT/CP</td>
<td>10</td>
<td>0.25</td>
<td>247</td>
<td>1M KOH</td>
<td>J. Am. Chem. Soc. 2013, 135, 8452</td>
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<tr>
<td>Ni$<em>{0.08}$FeAl$</em>{0.91-}$ LDHs/NF</td>
<td>20</td>
<td>-</td>
<td>304</td>
<td>1M KOH</td>
<td>Nano Energy 2017, 35, 350.</td>
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<tr>
<td>NiFeMn LDH/CP</td>
<td>20</td>
<td>~0.20</td>
<td>289</td>
<td>1M KOH</td>
<td>Chem. Commun. 2016, 52, 908</td>
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<td>Fe-Ni$_3$S$_2$/FeNi foil</td>
<td>10</td>
<td>-</td>
<td>282</td>
<td>1M KOH</td>
<td>Small, 2017, 13, 1604161.</td>
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<tr>
<td>Sample</td>
<td>Rs</td>
<td>Rct</td>
<td>CPE</td>
<td></td>
<td></td>
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<td>--------------------------------</td>
<td>-----</td>
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<tr>
<td>NiFe-LDHs/CP</td>
<td>0.05</td>
<td>0.67</td>
<td>0.04</td>
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<td>BA-NiFe-LDHs/CP</td>
<td>0.16</td>
<td>2.11</td>
<td>0.12</td>
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**Table S2** Geometric values of the electronic elements estimated from electrical Equivalent

**Reference**