Electronic Supplementary Information

Needle Grass-like Cobalt Hydrogen Phosphate on Ni Foam as Effective and Stable Electro catalysts for Oxygen Evolution Reaction

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Experimental section

Preparation of CoHPO/NF electrode

4 mmol K$_2$HPO$_4$·3H$_2$O, 4 mmol CoSO$_4$·7H$_2$O and 2 mmol CON$_2$H$_4$ were added and dissolved in 80 mL deionized H$_2$O. After 10 minutes ultrasound, the solution and the Ni foam were transferred to a Teflon-lined autoclave and then it was heated at 120 °C for 12 h. The powder in the Teflon-lined autoclave was collected and washed via water and ethanol. The CoHPO/NF electrode was ultrasoninated with water and ethanol several times. Both powder and CoHPO/NF electrode were dried at 80 ºC overnight.

Preparation of Co(OH)$_2$/NF electrode

The preparation of Co(OH)$_2$/NF was similar to that of CoHPO/NF, except for the addition of K$_2$HPO$_4$·3H$_2$O.

Preparation of RuO$_2$-NF electrode

RuO$_2$ (4 mg) was dispersed in a 1 mL mixed solution, including 490 μL H$_2$O, 15 μL Nafion solution (5 wt %), and 495 μL EtOH, and then followed by sonication to form a uniform catalyst ink. Put the as-prepared ink (100 μL) on the Nickel Foam (area: 1 cm×1 cm). Finally, the electrode was dried at 80 ºC overnight.

Preparation of CoHPO -NF electrode

CoHPO (4 mg) was dispersed in a 1 mL mixed solution, including 490 μL H$_2$O, 15 μL Nafion solution (5 wt %), and 495 μL EtOH, and then followed by sonication to form a uniform catalyst ink. Put the as-prepared ink (100 μL) on the Nickel Foam (area: 1 cm×1 cm). Finally, the electrode was dried at 80 ºC overnight.

Preparation of CoHPO /CP electrode
The preparation of CoHPO/CP was similar to that of CoHPO/NF, except for replacing nickel foam with carbon Paper (CP).

Materials characterization

The morphologies were tested through Hitachi field emission scanning electronic microscope. Micromorphology and fine structure were measured via FEI Tecnai F20 field emission transmission electron microscope. The crystal structure was confirmed by Phillips X’pert ProMPD diffractometer. Nicolet-380 Fourier transform infrared spectrometer was used to test Fourier transform infrared spectroscopy (FT-IR). An ESCALAB 250Xi spectrometer (Thermo Fisher) was employed to measure the X-Ray photoelectron spectra (XPS). The loading of CoHPO was measured using inductively coupled plasma mass spectroscopy (Thermo XSeries II) by dissolving 1 cm × 1 cm electrode in 100 mL aquaregia.

Electrochemical measurements

Zennium IM6 station was applied to conduct electrochemical measurements in 1.0 M KOH. The linear sweep voltammetry (LSV) curves were scanned at 5 mV s⁻¹ in a standard three-electrode system. The Pt wire and Hg/HgO electrode acted as the counter electrode and the reference electrode, and as-prepared Ni Foam was the working electrode. The conversion of the potential value to reversible hydrogen electrode (RHE) was based on the formula: \( \eta = E_{\text{RHE}} - 1.23 \) V. Electrochemical impedance spectroscopy (EIS) was measured in the frequency range from 10 mHz to 100 kHz.

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 were calculated by the strongly constrained and appropriately normed (SCAN) functional within the meta-generalized-gradient approximation (meta-GGA). A plane-wave basis set was used with kinetic energy cutoff of 400 eV with a K-point grid of 2×2×4 and 4×4×4 for CoHPO and Co(OH)$_2$, respectively, using the Gamma centered method. 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 CHPO and Co(OH)$_2$ were created and cut alone the (001) direction. To avoid the interaction between two neighboring images, the vacuum space along the z axis was set to be 10 Å.

The adsorption energies of OH groups on two substrates were defined as:

$$E_{\text{ads}} = E_{\text{system}} - E_{\text{substrate}} - E_{\text{OH}}$$

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

![XRD of CoHPO/NF and Co(OH)$_2$/NF](image)

**Figure S1.** XRD of CoHPO/NF and Co(OH)$_2$/NF
Figure S2. SEM of Co(OH)$_2$ at low (a) and high (b) magnification

Figure S3. Polarization curves of CoHPO/NF, Co(OH)$_2$/NF, CoHPO-NF, CoHPO/CP, RuO$_2$-NF, NF and Carbon paper.
Figure S4 CVs of Co(OH)$_2$/NF (a) and CoHPO/NF (b) in the non-faradaic capacitance current range at scan rates of 10, 20, 40, 60, 80, and 100 mV s$^{-1}$.

Figure S5 XPS Co spectra of the CoHPO/NF for initial electrode and after OER durability tests.
Figure S6 TEM (a) and HRTEM (b) for CoHPO after OER durability tests.

Figure S7 The crystal structure of the Co(OH)$_2$ and corresponding structure with ELF isosurfaces
**Figure S8** The pH value-time curve with CoHPO and Co(OH)$_2$ added in the fifth min (the same weight CoHPO and Co(OH)$_2$ powder in the same volume of solution (0.1 mg/ml)).

**Table S1** the ICP for initial CoHPO/NF and Co(OH)$_2$/NF after OER test

<table>
<thead>
<tr>
<th>Sample</th>
<th>CoHPO/NF</th>
<th>Co(OH)$_2$/NF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co (μg ml$^{-1}$)</td>
<td>1.21</td>
<td>2.44</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$j$(mAcm$^{-2}$)</th>
<th>$\eta$(mV)</th>
<th>Electrolyte</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoHPO/NF</td>
<td>50</td>
<td>350</td>
<td>1M KOH</td>
<td>This work</td>
</tr>
<tr>
<td>CoHPO/NF</td>
<td>100</td>
<td>395</td>
<td>1M KOH</td>
<td>This work</td>
</tr>
<tr>
<td>CoFe-LDH</td>
<td>50</td>
<td>360</td>
<td>1M KOH</td>
<td>Chem. Sci., 2015, 6, 6624.</td>
</tr>
<tr>
<td>Co@Co$_3$O$_4$–NC</td>
<td>10</td>
<td>391</td>
<td>1M KOH</td>
<td>J. Mater. Chem. A, 2017, 5, 9533-9536</td>
</tr>
<tr>
<td>CoSe$_2$-NC</td>
<td>50</td>
<td>450</td>
<td>1M KOH</td>
<td>ACS Appl. Mater. Interfaces 2019, 11, 3372</td>
</tr>
<tr>
<td>Sample</td>
<td>Initial</td>
<td>After durability tests</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------------------------------</td>
<td>---------</td>
<td>------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiCo LDHs</td>
<td>50</td>
<td>430</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co&lt;sub&gt;5&lt;/sub&gt;Mn-LDH/MWCNT</td>
<td>50</td>
<td>410</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu&lt;sub&gt;0.3&lt;/sub&gt;Co&lt;sub&gt;2.7&lt;/sub&gt;P/NC</td>
<td>50</td>
<td>~350</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu@NCNT/Co&lt;sub&gt;x&lt;/sub&gt;O&lt;sub&gt;y&lt;/sub&gt;</td>
<td>10</td>
<td>370</td>
<td></td>
<td></td>
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</tbody>
</table>

**Table S3** the ICP for initial and after durability tests CoHPO/NF.