Electronic Supplementary Information (ESI) for

Ni (II)-Doped Anionic Metal-organic Framework Nanowire Arrays for Enhancing Oxygen Evolution Reaction

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Part I: Experimental Section

1. Structural determination

All powder X-ray diffraction (PXRD) analyses were tested by a Rigaku Dmax2500 diffractometer with Cu Kα radiation using a step size of 0.05°. Fourier transform infrared (FT-IR) spectra were taken on a Nicolet Magna 750 FT–IR spectrometer in the 4000–500 cm⁻¹ region by using KBr pellets.

2. Electrochemical characterization

OER measurements were performed in a three-electrode glass cell. All the electrochemical data were conducted at room temperature on CHI760 D in 1.0 M KOH. Electrochemical impedance spectroscopy (EIS) measurements were tested by applying an AC voltage with 5 mV amplitude in a frequency range from 1000000 to 1 Hz. The collected results were adjusted with iR correction to decrease the influence of ohmic resistance. The synthesized samples grown on a substrate (e.g., Cu foam 0.8cm x0.8 cm) were used as the working electrode for electrochemical characterizations. The current density in this work was normalized to the geometrical surface area and the measured potentials vs. Ag/AgCl were converted to a reversible hydrogen electrode (RHE) scale according to the Nernst equation ($E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \times \text{pH} + 0.213$). To ensure the O₂/H₂O equilibrium at 1.23 V vs. RHE, the flow of N₂ was maintained over the electrolyte (1.0 MKOH) during electrochemical measurements in order. The polarization curves were recorded with the scan rate of 5 mV s⁻¹. The working electrodes were scanned for several times before the stable polarization curves were collected.

The Tafel slope was calculated according to Tafel equation as follows:

$$\eta = b \cdot \log\left(\frac{j}{j_0}\right)$$

$\eta$: the overpotential,

$b$: the Tafel slope,

$j$: the current density,

$j_0$: the exchange current density.

The onset potentials were determined based on the beginning of the linear region in the Tafel plots.
3. Synthesis of JXUN-4

A mixture of Zn(NO$_3$)$_3$·6H$_2$O (31 mg), adenine (7mg), and 4,4’ -biphenyldicarboxylic acid (13mg) in a N, N-dimethylformamide (DMF; 5mL) / water (H$_2$O; 1mL) solution were placed in a 20 mL vial. The vessel heated at 120 °C for 3 days, and then cooled to room temperature. Crystalline samples were filtered, washed with DMF, distilled water and ethanol, and then dried at ambient temperature.

4. JXUN-4 grown on Cu foam (JXUN-4 -NA/CF)

Firstly, a Cu foam was cleaned with absolute ethanol and Milli-Q water through ultrasonication method and was placed in a 20 mL vial. Secondly, A mixture of Zn(NO$_3$)$_3$·6H$_2$O (31 mg), adenine (7mg), and 4, 4’ -biphenyldicarboxylic acid (13mg) in a DMF(6mL) / water (7mL) solution were placed in a 20 mL vial, which was heated at 120 °C for 72 hours, and then cooled down to room temperature at a rate of 5°C h$^{-1}$, the Cu foam with attached nanowire array (JXUN-4 -NA/CF) was obtained.

5. Synthesis of Ni@JXUN-4-NA on Cu foam (Ni@JXUN-4-NA-CF)

The fresh JXUN-4 -NA/CF was successively washed with DMF, H$_2$O and methanol before immersing it in Ni(NO$_3$)$_2$ (50 mM) solution for 18, 10, and 2h, respectively. The Ni (II) ions were captured and doped in the anionic structure of JXUN-4-NA/CF. Further, Energy-dispersive X-ray spectroscopy (EDS) measurement demonstrated Ni contents were, respectively, 4.6, 2.8 and 0.5 %.

6. Ni@JXUN-4 coated on Cu Foam (Ni@JXUN-4/CF)

The as-synthesized JXUN-4 crystals were washed with distilled water and methanol before immersion in Ni(NO$_3$)$_2$ (50 mM) for 18h. The Ni$^{2+}$ ions were captured in the framework of anionic MOFs (Ni@JXUN-4/CF). Further, ICP measurement demonstrated Ni contents was 5.0 %. The as-synthesized Fe@JXUN-4/CF was ultrasonically dispersed in the mixture of 1 mL of Milli-Q water and ethanol, and then transferred onto Cu foam with a loading amount of ~ 0.26 mg cm$^{-2}$. The obtained electrode was subjected to overnight solvent evaporation at room temperature, subsequent coating with mixed Nafion solution (0.05 wt.%).
8. JXUN-4 coated on Cu Foam (JXUN-4/CF)
The procedure for preparation of JXUN-4/CF was the same as that for Ni@JXUN-4/CF except for using JXUN-4 instead of Ni@JXUN-4.

9. Preparation of RuO₂ electrode on Cu foam (RuO₂/CF)
The procedure for preparation of RuO₂/CF was the same as that for JXUN-4/CF except for using RuO₂ instead of JXUN-4.
Part II: Supplementary Results

**Figure S1.** The PXRD patterns of Ni@JXUN-4 based samples under different conditions.

**Figure S2.** The N$_2$ sorption isotherms of Ni@JXUN-4.
Figure S3. Chronoamperometric curves for Ni@JXUN-4-NA/CF electrocatalyst at a fixed overpotential of 0.52 V(Ag/AgCl).

Figure S4. FT-IR patterns of Ni@JXUN-4-NA/CF electrocatalyst before and after OER stability test.
**Figure S5.** LSV plots of Ni@JXUN-4-NA/CF electrocatalyst before and after a 12 h stability test.

**Figure S6.** LSV plots of Ni@JXUN-4/CF and JXUN-4/CF electrocatalyst.
Figure S7. Linear relationship of the current density at 1.1 V (vs. RHE) vs. scan rates for Ni@JXUN-4-NA/CF (black line) and JXUN-4-NA/CF (red line).
Table S1. Comparison of electrocatalytic OER activities for Ni@JXUN-4-NA/CF with reported MOFs-based electrocatalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Over-potential</th>
<th>Substrate</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co/MIL-100(Fe)</td>
<td>734 at 5 mA cm⁻²</td>
<td>GCE</td>
<td><em>Int. J. Hydrogen Energy, 2014, 39,16179</em></td>
</tr>
<tr>
<td>Co-ZIF-9</td>
<td>510 at 1 mA cm⁻²</td>
<td>FTO</td>
<td><em>Nanoscale, 2014, 6, 9930</em></td>
</tr>
<tr>
<td>NU-1000</td>
<td>566 at 10 mA cm⁻²</td>
<td>FTO</td>
<td><em>ACS Appl. Mater. Interfaces 2015, 7, 28223</em></td>
</tr>
<tr>
<td>MAF-X27-OH</td>
<td>292 at 10 mA cm⁻²</td>
<td>Cu Foil</td>
<td><em>J. Am. Chem. Soc., 2016, 138, 8336</em></td>
</tr>
<tr>
<td>Co-WOC-1</td>
<td>390 at 1 mA cm⁻²</td>
<td>GCE</td>
<td><em>Angew. Chem. Int. Ed., 2016, 55, 2425</em></td>
</tr>
<tr>
<td>Ni/Fe-BTC</td>
<td>270 at 10 mA cm⁻²</td>
<td>NF</td>
<td><em>ACS Appl. Mater. Interfaces, 2016, 8, 16736</em></td>
</tr>
<tr>
<td>Titanium carbide-CoBDC</td>
<td>410 at 10 mA cm⁻²</td>
<td>GCE</td>
<td><em>ACS Nano, 2017, 11,5800</em></td>
</tr>
<tr>
<td>Ni-MOF</td>
<td>320 at 100 mA cm⁻²</td>
<td>NF</td>
<td><em>Inorg. Chem. Front., 2018, 5, 1570</em></td>
</tr>
<tr>
<td>CoZIF-9(III)</td>
<td>380 at 10 mA cm⁻²</td>
<td>NF</td>
<td><em>Adv. Sci. 2018, 5, 1801029</em></td>
</tr>
<tr>
<td>NiFe-MOF-74</td>
<td>223 at 10 mA cm⁻²</td>
<td>NF</td>
<td><em>Chem. Commun., 2018, 54, 7046</em></td>
</tr>
<tr>
<td><strong>Ni@JXUN-4-NA</strong></td>
<td><strong>310 at 20 mA cm⁻²</strong></td>
<td><strong>CF</strong></td>
<td><strong>This work</strong></td>
</tr>
</tbody>
</table>

CF: Cu foam, NF: Ni foam, GCE: glassy carbon electrode