Electronic Supplementary Information

Structural and Electronic Modulation of Conductive MOFs for Efficient Oxygen Evolution Reaction Electrocatalysis

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1. Experimental Section

**TOF calculation:** The TOF values were estimated based on our previous report, resulting in the following formula:

$$\text{TOF} = \frac{\text{number of total oxygen turnovers / cm}^2}{\text{number of active sites / cm}^2}$$

The number of total oxygen turnovers was calculated from the current density by the following equation:

$$\text{Number of } O_2 = \left( \frac{1 \text{ mA}}{1000 \text{ mA} \cdot \text{cm}^2} \right) \left( \frac{1 \text{ mol e}^-}{96485.3 \text{ C}} \right) \left( \frac{1 \text{ mol } O_2}{4 \text{ mol } e^-} \right) \left( \frac{6.022 \times 10^{23} \text{ molecules}}{1 \text{ mol } O_2} \right) = 1.56 \times 10^{15} \frac{O_2/\text{s}}{\text{cm}^2 \text{ per mA/cm}^2}$$

The number of active sites was regarded as the number of surface sites (Ni-O$^4_4$ and Fe-O$^4_4$ are regarded as active sites), and calculated by the following formula:

$$\text{Number of active sites} = \left( \frac{\text{number of metal sites / unit cell}}{\text{Volume / unit cell}} \right)^2$$

Finally, the plot of current density can be converted into a TOF plot according to the following formula:

$$\text{TOF} = \left( \frac{1.56 \times 10^{15} \frac{O_2}{\text{s/cm}^2 \text{ per mA/cm}^2}}{\text{Number of active sites} \times A_{\text{ECSA}}} \right) \times |J|$$

The $A_{\text{ECSA}}$ is the electrochemical active surface area, which can be calculated from the following formula, where specific capacitance is $C_{dl}$, and 40 μF cm$^{-2}$ is a constant to convert capacitance to $A_{\text{ECSA}}$:

$$A_{\text{ECSA}} = \frac{\text{specific capacitance}}{40 \text{ μF cm}^{-2} \text{ per cm}^2_{\text{ECSA}}}$$

**D-band center Analysis:** The d-band center ($\varepsilon_d$) was calculated according to following equation:

$$\varepsilon_d = \frac{\int_{-\infty}^{0} N(\varepsilon) \varepsilon \, d\varepsilon}{\int_{-\infty}^{0} N(\varepsilon) \, d\varepsilon}$$

Where $N(\varepsilon)$ is the d-band DOS, $\varepsilon$ is the energy.
2. PXRD Patterns

![Figure S1](image1.png)

**Figure S1.** Experimental (green) and simulated (grey) PXRD pattern of NiPc-Ni MOF.

![Figure S2](image2.png)

**Figure S2.** Experimental PXRD patterns of NiPc-NiFe$_{0.05}$, NiPc-NiFe$_{0.09}$, NiPc-NiFe$_{0.20}$, and simulated pattern of NiPc-NiFe$_{0.50}$. 
3. SEM and TEM Images

Figure S3. SEM images (a, b) of NiPc-Fe, SEM (c) and TEM (d) image of NiPc-Ni.
Figure S4. TEM images of NiPc-NiFe0.05 (a, b), NiPc-NiFe0.09 (c, d), NiPc-NiFe0.20 (e, f), NiPc-Fe (g, h).
4. XPS Spectra

Figure S5. XPS spectra of NiPc-NiFe$_{0.09}$: a) survey, b) C 1s, c) N 1s, d) O 1s. There is an integral ratio of 55:45 for C=O : C-O.

Figure S6. XPS spectra of NiPc-NiFe$_{0.05}$: a) survey, b) C 1s, c) N 1s, d) O 1s. There is an integral ratio of 47:53 for C=O : C-O.
Figure S7. XPS spectra of NiPc-NiFe$_{0.20}$: a) survey, b) C 1s, c) N 1s, d) O 1s. There is an integral ratio of 51:49 for C=O : C-O.

Figure S8. XPS spectra of NiPc-Fe: a) survey, b) C 1s, c) N 1s, d) O 1s, e) Ni 2p, f) Fe 2p. There is an integral ratio of 56:44 for C=O : C-O.
5. Linear Sweep Voltammetry

Figure S10. Enlarged LSV plots for OER.
6. ECSA Measurements

Figure S11. Scan rate dependent-current densities at 0.92 V vs. RHE

Figure S12. CVs in non-faradaic region of four MOFs.
7. Stability Test

Figure S13. Chronopotentiometry test of NiPc-NiFe$_{0.09}$@CC (Carbon Cloth).

Figure S14. High-resolution Ni 2p XPS spectra before and after Chronopotentiometry test of NiPc-NiFe$_{0.09}$@CC.
Figure S15. (a) LSV curves of NiPc-NiFe$_{0.09}$ after 3000 CV cycles, (b) PXRD patterns of NiPc-NiFe$_{0.09}$ before and after OER process, (c, d) SEM images of NiPc-NiFe$_{0.09}$ after OER process (3000 CV cycles).
8. Comparison with Commercial Catalyst

**Figure S16.** LSV curves of NiPc-NiFe$_{0.09}$ and commercial RuO$_2$ catalyst before and after 1000 CV cycles, the values in the figure are the shift of $\eta$ @10 mA cm$^{-2}$ after 1000 CV cycles. Besides, the $\eta$ of RuO$_2$ is 317 mV @10 mA cm$^2$, which is larger than that of NiPc-NiFe$_{0.09}$, indicating the superior OER electrocatalytic performance of NiPc-NiFe$_{0.09}$. 
9. Theoretical Calculation Model

Figure S17. Constructed MOF Slabs for calculation.
Table S1. Comparisons of the OER activity of MOF-based catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>$\eta$ @ $j=10$ mA cm$^{-2}$ (mV)</th>
<th>$\eta$ @ $j=100$ mA cm$^{-2}$ (mV)</th>
<th>Tafel slope (mV dec$^{-1}$)</th>
<th>TOF (s$^{-1}$)</th>
<th>Substrate</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiPe-NiFe$_{0.09}$</td>
<td>1.0 M KOH</td>
<td>300</td>
<td>384</td>
<td>55</td>
<td>1.943 @$\eta$=300 mV</td>
<td>GC</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>11.943 @$\eta$=350 mV</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MAF-X27-OH</td>
<td>1.0 M KOH</td>
<td>387</td>
<td>-</td>
<td>66</td>
<td>0.0014 @$\eta$=300 mV</td>
<td>GC</td>
<td>J. Am. Chem. Soc., 2016, 138, 8336.</td>
</tr>
<tr>
<td>Ni-HAB</td>
<td>1.0 M KOH</td>
<td>320</td>
<td>-</td>
<td>51</td>
<td>0.016 @$\eta$=300 mV</td>
<td>CFP</td>
<td>Small, 2020, 16, 1907043.</td>
</tr>
<tr>
<td>NiCo-UOMOFNs</td>
<td>1.0 M KOH</td>
<td>250</td>
<td>-</td>
<td>42</td>
<td>0.86 @$\eta$=300 mV</td>
<td>GC</td>
<td>Nat. Energy., 2016, 1, 16184.</td>
</tr>
<tr>
<td>Pb-TCPP</td>
<td>1.0 M KOH</td>
<td>470</td>
<td>-</td>
<td>106.2</td>
<td>0.00051 @$\eta$=1.2 V</td>
<td>GC</td>
<td>Dalton Trans., 2016, 45, 61-65.</td>
</tr>
<tr>
<td>CUMSs-ZIF-67</td>
<td>1.0 M KOH</td>
<td>410</td>
<td>-</td>
<td>185.1</td>
<td>0.462 @$\eta$=300 mV</td>
<td>GC</td>
<td>Nano Energy, 2017, 41, 417-425.</td>
</tr>
<tr>
<td>UTSA-16</td>
<td>1.0 M KOH</td>
<td>408</td>
<td>710*</td>
<td>77</td>
<td>-</td>
<td>GC</td>
<td>ACS Appl. Mater. Interfaces, 2017, 9, 7193-7201.</td>
</tr>
<tr>
<td>CoNi-Cu(BDC)</td>
<td>1.0 M KOH</td>
<td>327</td>
<td>420*</td>
<td>75.7</td>
<td>-</td>
<td>GC</td>
<td>New J. Chem., 2020, 44, 2459-2464.</td>
</tr>
<tr>
<td>Ni$<em>{5.7}$Ru$</em>{0.3}$[HHTP]$_3$</td>
<td>0.1 M KOH</td>
<td>390</td>
<td>-</td>
<td>61</td>
<td>-</td>
<td>GC</td>
<td>Chem. Commun., 2020, 56, 13615-13618.</td>
</tr>
<tr>
<td>NNU-23</td>
<td>0.1 M KOH</td>
<td>365</td>
<td>-</td>
<td>81.8</td>
<td>0.03 @$\eta$=400mV</td>
<td>CC</td>
<td>Angew. Chem. Int. Ed., 2018, 57, 9660-9664.</td>
</tr>
</tbody>
</table>

*These values are estimated by LSV plots in the literatures.
11. Equivalent Circuit Parameters for EIS Analysis

Table S2. Fitting Results of these conductive MOFs.

<table>
<thead>
<tr>
<th>MOF Type</th>
<th>$R_s$ ($\Omega \text{ cm}^2$)</th>
<th>CPE ($\text{mF cm}^{-2}$)</th>
<th>$R_p$ ($\Omega \text{ cm}^2$)</th>
<th>$C_{dl}$ ($\text{mF cm}^{-2}$)</th>
<th>$R_{ct}$ ($\Omega \text{ cm}^2$)</th>
<th>$Z_o$ ($\text{S s}^{0.5} \text{cm}^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiPc-NiFe$_{0.09}$</td>
<td>0.8756</td>
<td>0.3521</td>
<td>0.05715</td>
<td>86.92</td>
<td>0.3315</td>
<td>0.1189</td>
</tr>
<tr>
<td>NiPc-NiFe$_{0.05}$</td>
<td>0.7179</td>
<td>1.726</td>
<td>0.139</td>
<td>26.62</td>
<td>1.557</td>
<td>0.1055</td>
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<tr>
<td>NiPc-NiFe$_{0.20}$</td>
<td>0.949</td>
<td>0.1827</td>
<td>0.1603</td>
<td>1.594</td>
<td>2.319</td>
<td>0.02773</td>
</tr>
<tr>
<td>NiPc-Fe</td>
<td>0.7634</td>
<td>1.225</td>
<td>3.953</td>
<td>1.078</td>
<td>12.26</td>
<td>0.1232</td>
</tr>
<tr>
<td>NiPc-Ni</td>
<td>0.7638</td>
<td>427.2</td>
<td>0.3281</td>
<td>40.17</td>
<td>19.25</td>
<td>0.3553</td>
</tr>
</tbody>
</table>

In the applied module, $R_s$ represents solution resistance, which a combination of contact resistance in the overall circuit and electrolyte. CPE represents the constant phase elements. $R_p$ and $R_{ct}$ are on behalf of the resistance of surface porosity and charge-transfer resistance, respectively. $C_{dl}$ represents the double-layer capacitance, which is formed by the adsorption of ions in the solution onto the surface of the electrode. $Z_o$ is limited Warburg impedance, which is originated from finite diffusion layer (such as a thin cell or a coated sample).

The similar value of $R_s$ indicates the conditions of our electrochemical tests are constant. The small value of $R_p$ of NiPc-NiFe$_{0.09}$ demonstrates that this catalyst is highly porous. The value of $C_{dl}$ of NiPc-NiFe$_{0.09}$ is significantly larger than other MOFs, in accordance with its highest electrocatalytic performance. $R_{ct}$ value reflects the ability of charge transfer between electrolyte and electrode. The smallest value of 0.3315 $\Omega \text{ cm}^2$ of NiPc-NiFe$_{0.09}$ proves the highest electron transport efficiency.

References: