Amorphous FeNi-bimetallic Infinite Coordination Polymers as Advanced Electrocatalysts for the Oxygen Evolution Reaction

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Experimental Section

Materials

All chemicals used in this work were analytical grade and without further purification. 2-aminoterephthalic acid (H$_2$BDC-NH$_2$), 1,4-benzenedicarboxylate (H$_2$BDC), 1,4-naphthalenedicarboxylic acid (H$_2$(1,4-NDC)), 2,6-naphthalenedicarboxylic acid (H$_2$(2,6-NDC)), 2,5-dihydroxynaphthallic acid (H$_2$DOBDC), trimedic acid (H$_3$BTC) were purchased from Energy Chemical. Iron chloride tetrahydrate (FeCl$_2$·4H$_2$O) were purchased from Tianjin bailunsi biotechnology Co. Ltd. Nickel (II) acetate tetrahydrate [(CH$_3$COO)$_2$Ni·4H$_2$O], ethanol (C$_2$H$_5$OH), acetonitrile (CH$_3$CN) and N,N-dimethylformamide (DMF) were purchased from Sinopharm Chemical Reagent Co. Ltd.

Synthesis of bimetallic Fe$_x$Ni$_y$(BDC-NH$_2$) ICPs

Take the synthesis of Fe$_1$Ni$_2$(BDC-NH$_2$) ICP as a typical example. 0.09 mmol of FeCl$_2$·4H$_2$O (17.9 mg) and 0.18 mmol of (CH$_3$COO)$_2$Ni·4H$_2$O (44.8 mg) were dissolved in a 30 mL mixture of DMF and CH$_3$CN (V:V=1:2) as the metal precursor solution. The organic ligand solution was dissolving 0.39 mmol of H$_2$BDC-NH$_2$ (70.6 mg) into the mixture of 20 ml of DMF and 10 ml of CH$_3$CN. Then the metal precursor solution was directly added into linker solution under magnetic stirring 1 h at room temperature. As time goes by, the deep yellow precipitation was gradually increasing. Finally, the product was centrifuged and washed with DMF three times to obtain Fe$_1$Ni$_2$(BDC-NH$_2$) ICP. The synthesis of the Fe$_x$Ni$_y$(BDC-NH$_2$) ICPs with diverse metallic ratios only need to adjust the ions concentrations of FeCl$_2$·4H$_2$O and
(CH₃COO)₂Ni·4H₂O. At the same time, the preparation method and all ions concentrations of other FeNi-bimetallic ICPs with different ligands were consistent with the above method.

**Preparation of catalytic electrodes**

The products were uniformly dispersed into 5 ml ethanol. Ni foam substrates were impregnated directly into the teflon cap of containing 2.2 ml samples. Then put them in the air and make the solvent volatilize completely at the room temperature.

**Characterization**

The morphology of Fe₁Ni₂(BDC-NH₂) ICP was characterized with a field emission scanning electron microscope (FE-SEM, Hitachi SU8010) and corresponding elemental mapping images were captured on energy-dispersive X-ray (EDX, Oxford Instruments). The crystal structure of the product was tested by X-ray diffraction (XRD) on PANalytical Empyrean X-ray diffractometer in the 2θ range of 5−40° with Cu Kα1 (λ = 1.5406 Å) radiation. The X-ray photoelectron spectroscopy (XPS) measurements were carried out on Thermo Scientific ESCALAB 250 apparatus to affirm elemental valence states of the electrocatalyst. The organic groups and specific surface areas/pore sizes of the samples were characterized by fourier transform infrared spectroscopy (FT-IR, Bruker VERTEX 70) and nitrogen adsorption-desorption isotherms at 77 K (Micromeritics ASAP 2020 system). The actual ratio of Fe and Ni content in the Fe₁Ni₂(BDC-NH₂) was measured by the inductively coupled plasma-optical emission spectroscopy (ICP-OES) on a PerkinElmer Optima 2100DV ICP-OES spectrometer.
ICP-OES measurement

The sample of Fe$_1$Ni$_2$(BDC-NH$_2$), where the feeding ratio of Fe to Ni is 1:2, was measured by ICP-OES, indicating the mole ratio of Fe to Ni in the sample is 1:2.45.

Electrochemical Test

The electrochemical performance of catalytic electrodes was measured by electrochemical workstation (CHI660E, Shanghai Chenhua Instrument Co., Ltd.). The linear sweep voltammetry (LSV) was performed by sweeping the potential from 1.0 V to 1.8 V at a scan rate of 5 mV s$^{-1}$. Electrochemical impedance spectroscopy (EIS) was carried out at the polarization potential 1.53 V. The electrochemical double layer capacitance (C$_{dl}$) was obtained by cyclic voltammetry (CV) in a region of non-Faradaic (0.2 V-0.3 V vs. Ag/AgCl) at different scan rates of 20, 40, 60, 80, 100, 120 mV s$^{-1}$, respectively. The stability tests were proceeded from chronoamperometry (j-t) at a constant voltage of 0.49 V vs.Ag/AgCl for 12 hours and the comparison of LSV curves after 1000 CV cycles at a sweep rate of 20 mV s$^{-1}$.

RHE calibration

We used the Ag/AgCl electrode as the reference electrode in all measurements. The potentials reported here were calibrated with respect to the reversible hydrogen electrode (RHE). The calibration was performed in H$_2$-saturated 1.0 mol/L KOH and Pt sheets were used as working and counter electrodes. CV curve was measured at scan rate of 1 mV·s$^{-1}$ and the average of two potentials at 0 mA current was taken to be the thermodynamic potential for the hydrogen electrode reactions.
Fig. S1 AFM image of as-prepared Fe₁Ni₂(BDC-NH₂) ICP nanosheets.

Fig. S2 CV curve of hydrogen electrode reaction.

So the 1 M KOH, E (RHE) = E (Ag/AgCl) + 1.0247V.
**Fig. S3** LSV curves of Fe\textsubscript{1}Ni\textsubscript{2}(BDC-NH\textsubscript{2})/NF with different loading amounts.

**Fig. S4** LSV curves of Fe\textsubscript{1}Ni\textsubscript{2} bimetallic ICPs/NF electrodes with different ligands.
**Fig. S5** Tafel plots of Fe$_1$Ni$_2$ bimetallic ICP/NF electrodes with different ligands.

**Fig. S6** The $C_{dl}$ of Fe$_x$Ni$_y$(BDC-NH$_2$)/NF with different ratios of Fe and Ni.

The $C_{dl}$ value of the Fe$_x$Ni$_y$(BDC-NH$_2$)/NF with 1:2 ratio is confirmed to be 17.16 mF·cm$^{-2}$, which is higher than the other electrodes with ratios of 3:1 (10.83 mF·cm$^{-2}$).
2:1 (12.63 mF·cm\(^{-2}\)), 1:1 (13.69 mF·cm\(^{-2}\)) and 1:3 (14.91 mF·cm\(^{-2}\)).

Fig. S7 SEM image of Fe\(_1\)Ni\(_2\)(BDC-NH\(_2\))/NF after stability measurement of OER.

Fig. S8 XRD pattern of Fe\(_1\)Ni\(_2\)(BDC-NH\(_2\)) ICP after stability measurement of OER.
**Fig. S9** High-resolution XPS spectra of (a) Fe 2p and (b) Ni 2p of Fe\textsubscript{1}Ni\textsubscript{2}(BDC-NH\textsubscript{2}) ICP after stability measurement of OER.

**Fig. S10** High-resolution Ni 2p XPS spectra of Ni(BDC-NH\textsubscript{2}) and Fe\textsubscript{1}Ni\textsubscript{2}(BDC-NH\textsubscript{2}).
Table S1 The OER catalytic performances comparison of the recently reported catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Overpotential (mV)</th>
<th>Tafel slope (mV dec^{-1})</th>
<th>Electrolyte</th>
<th>Reference</th>
</tr>
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<tbody>
<tr>
<td>Fe_{0.5}Ni_{0.5}(BDC-NH_2)</td>
<td>228 @ 10 mA·cm^{-2}</td>
<td>30.3</td>
<td>1 M KOH</td>
<td>This work</td>
</tr>
<tr>
<td>CoSe_2@DG composite</td>
<td>270 @ 10 mA·cm^{-2}</td>
<td>64</td>
<td>0.1 M KOH</td>
<td>1</td>
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<tr>
<td>o-CoSe_2-O UNs</td>
<td>251 @ 10 mA·cm^{-2}</td>
<td>73</td>
<td>1 M KOH</td>
<td>2</td>
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<tr>
<td>MIL-53(FeNi)/NF</td>
<td>233 @ 50 mA·cm^{-2}</td>
<td>31.3</td>
<td>1 M KOH</td>
<td>3</td>
</tr>
<tr>
<td>FeNi-O nanosheets</td>
<td>213 @ 10 mA·cm^{-2}</td>
<td>32</td>
<td>1 M KOH</td>
<td>4</td>
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<tr>
<td>FeNi_{1.34}@FeNi-foil</td>
<td>283 @ 10 mA·cm^{-2}</td>
<td>53</td>
<td>1 M KOH</td>
<td>5</td>
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<tr>
<td>Ni-MOF@Fe-MOF</td>
<td>265 @ 10 mA·cm^{-2}</td>
<td>82</td>
<td>1 M KOH</td>
<td>6</td>
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<tr>
<td>Fe_{0.9}Co_{0.1}@V_0.800</td>
<td>260 @ 10 mA·cm^{-2}</td>
<td>53</td>
<td>1 M KOH</td>
<td>7</td>
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<tr>
<td>MIL-100(FeNi)/NF</td>
<td>243 @ 10 mA·cm^{-2}</td>
<td>30.4</td>
<td>1 M KOH</td>
<td>8</td>
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<tr>
<td>NiFe-MOF-74</td>
<td>223 @ 10 mA·cm^{-2}</td>
<td>71.6</td>
<td>1 M KOH</td>
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<td>NiFe-MOF</td>
<td>240 @ 10 mA·cm^{-2}</td>
<td>34</td>
<td>0.1 M KOH</td>
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References: