Supporting Information

One-step growth of nitrogen-decorated iron-nickel sulfide nanosheets for oxygen evolution reaction

Yanshuo Jin¹, Xin Yue¹, Hongyu Du¹, Kai Wang¹, Shangli Huang², Pei Kang Shen*¹,²

¹ State Key Laboratory of Optoelectronic Materials and Technologies, School of Materials Science and Engineering, Sun Yat-sen University, Guangzhou 510275, P. R. China.

² Collaborative Innovation Center of Sustainable Energy Materials, Guangxi Key Laboratory of Electrochemical Energy Materials, State Key Laboratory of Processing for Non-ferrous Metal and Featured Materials, Guangxi University, Nanning 530004, P. R. China

AUTHOR INFORMATION

Corresponding Author

*pkshen@gxu.edu.cn; stsspk@mail.sysu.edu.cn
Experimental Section

Materials: Thiourea (CS(NH$_2$)$_2$, AR) and urea (CO(NH$_2$)$_2$, AR) were purchased from Tianjin Damao Chemical Reagent Factory. Sulfur (S, AR) was purchased from Aladdin Chemical Reagent Factory. Ni foams, NiFe alloy foams (Ni:85%; Fe:15%) and NiFe alloy foams (Ni:50%; Fe:50%) were purchased from Kunshan Jiayisheng Electronics Co., Ltd. Hydrochloric acid (HCl solution, 36-38%, AR) and potassium hydroxide (KOH, AR) were purchased from Guangzhou Chemical Reagent Factory. The deionized water was purified by the RO-DI system.

Synthesis of N-(Ni,Fe)$_3$S$_2$/NIF: 1 mmol thiourea was transferred into a corundum boat (60 mm×30 mm×15 mm). A piece of NiFe alloy foam (5.0 mm×2.0 mm×1.0 mm) after being cleaned by dilute HCl solution and deionized water was also transferred into the corundum boat. Then the corundum boat was transferred into a tube furnace. Annealing temperature is 300 °C for 1 hour. When cooled down to room temperature, N-(Ni,Fe)$_3$S$_2$/NIF was took out.

Synthesis of N-Ni$_3$S$_2$/NF: 1 mmol thiourea was transferred into a corundum boat (60 mm×30 mm×15 mm). A piece of Ni foam (5.0 mm×2.0 mm×1.0 mm) after being cleaned by dilute HCl solution and deionized water was also transferred into the corundum boat. Then the corundum boat was transferred into a tube furnace. Annealing temperature is 300 °C for 1 hour. When cooled down to room temperature, N-Ni$_3$S$_2$/NF was took out.

Synthesis of H:N-(Ni,Fe)$_3$S$_2$/NIF: 1 mmol sulfur and 1 mmol urea were transferred into a corundum boat (60 mm×30 mm×15 mm). A piece of NiFe alloy foam (5.0 mm×2.0 mm×1.0 mm) after being cleaned by dilute HCl solution and deionized water was also transferred into the corundum boat. Then the corundum boat was transferred into a tube furnace. Annealing temperature is 450 °C for 1 hour. When cooled down to room temperature, H:N-(Ni,Fe)$_3$S$_2$/NIF was took out.

Synthesis of N-(Ni,Fe)S/NIF: 1 mmol sulfur and 1 mmol urea were transferred into a corundum boat (60 mm×30 mm×15 mm). A piece of NiFe alloy foam (5.0 mm×2.0 mm×1.0 mm) after being cleaned by dilute HCl solution and deionized water was also transferred into the corundum boat. Then the corundum boat was transferred into a tube furnace. Annealing temperature is 300 °C for 1 hour. When cooled down to room temperature, N-(Ni,Fe)S/NIF was took out.

Synthesis of α-NiFeS/NIF: 1 mmol sulfur was transferred into a corundum boat (60 mm×30 mm×15 mm). A piece of NiFe alloy foam (5.0 mm×2.0 mm×1.0 mm) after being cleaned by dilute HCl solution and deionized water was also transferred into the corundum boat. Then the corundum boat was transferred into a tube furnace. Annealing temperature is 300 °C for 1 hour. When cooled down to room temperature, α-NiFeS/NIF was took out.

Synthesis of N-(Ni,Fe)$_3$S$_8$/NIF: 1 mmol thiourea was transferred into a corundum boat (60 mm×30 mm×15 mm). A piece of NiFe alloy foam (5.0 mm×2.0 mm×1.0 mm, Ni:50%; Fe:50%) after being cleaned by dilute HCl solution and deionized water was also transferred into the corundum boat. Then the corundum boat was transferred into a tube furnace. Annealing temperature is 300 °C for 1 hour. When cooled down to room temperature, N-(Ni,Fe)$_3$S$_8$/NIF was took out.
for 1 hour. When cooled down to room temperature, N-(Ni,Fe)$_3$S$_2$/NIF was took out.

Characterizations: TG-IR data were acquired on a TG-209/Vector$^{\text{TM}}$-22 combined instrument. SEM measurements were taken on a Quanta 400/INCA/HKL scanning electron microscope. XRD data were obtained on a D-MAX 2200 VPC diffractometer with Cu Ka radiation ($\lambda=1.54056$Å). TEM measurements were acquired on a JEM-2010HR electron microscopy. XPS measurements were carried out on an ESCALAB 250 spectroscopy.

Electrochemical measurements: Electrochemical measurements were tested on a Bio-logic VMP3 electrochemical analyzer. The OER electrochemical measurements were performed in a typical three-electrode device. The counter electrode is a graphite rod and the reference electrode is a reversible hydrogen electrode (RHE). Polarization curves at a scan rate of 1 mV s$^{-1}$ were measured in O$_2$-saturated 1 M KOH solution at 25 °C. The chronopotentiometric was used to test stability and the OER potential at a constant current density of 10 mA cm$^{-2}$. All of the potentials are iR-corrected.
Table S1. Comparisons of OER performance for various non-precious electrocatalysts in alkaline solution ($\eta_{10}$: overpotential at the current density of 10 mA cm$^{-2}$).

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>$\eta_{10}$ (mV)</th>
<th>Electrolyte</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-(Ni,Fe)$_3$S$_2$/NIF</td>
<td>167</td>
<td>1 M KOH</td>
<td>This work</td>
</tr>
<tr>
<td>FeCoW oxyhydroxides</td>
<td>191</td>
<td>1 M KOH</td>
<td>Science 2016, 352, 333.</td>
</tr>
<tr>
<td>W$<em>{0.5}$Co$</em>{0.4}$Fe$_{0.1}$/NF</td>
<td>250</td>
<td>1 M KOH</td>
<td>Angew. Chem. Int. Ed. 2017, 129, 4573.</td>
</tr>
<tr>
<td>Mn@Co$<em>x$Mn$</em>{3-x}$O$_4$</td>
<td>246</td>
<td>1 M KOH</td>
<td>Adv. Mater. 2017, 29, 1701820.</td>
</tr>
<tr>
<td>Fe-Ni$_3$S$_2$/FeNi</td>
<td>282</td>
<td>1 M KOH</td>
<td>Small, 2017, 13, 1604161.</td>
</tr>
</tbody>
</table>
Figure S1. TG curve of thiourea during the annealing process in a nitrogen atmosphere.

Figure S2. IR curve of decomposition products of thiourea in a nitrogen atmosphere.
Figure S3. SEM images of N-(Ni,Fe)$_3$S$_2$/NIF.

Figure S4. SEM images of N-Ni$_3$S$_2$/NF
Figure S5. TEM images of N-(Ni,Fe)$_3$S$_2$.

Figure S6. TEM images of N-Ni$_3$S$_2$. 
Figure S7. EDX elemental mapping images of N-(Ni,Fe)$_2$S$_2$. 
Figure S8. TG curve of urea during the annealing process in a nitrogen atmosphere.
Figure S9. SEM images of H:N-(Ni,Fe)$_3$S$_2$/NIF.

Figure S10. XRD pattern of H:N-(Ni,Fe)$_3$S$_2$/NIF.

Figure S11. TEM images of H:N-(Ni,Fe)$_3$S$_2$. 
**Figure S12.** SEM images of N-(Ni,Fe)S/NIF.

**Figure S13.** XRD pattern of N-(Ni,Fe)S/NIF.

**Figure S14.** TEM images of N-(Ni,Fe)S.
Figure S15. SEM images of α-NiFeS/NIF.

Figure S16. TEM images of α-NiFeS.
Figure S17. Current density @ 1.43 V vs. RHE and Electrochemical capacitance of N-(Ni,Fe)$_3$S$_2$/NIF, N-(Ni,Fe)S/NIF and α-NiFeS/NIF.
Figure S18. XRD patterns of N-(Ni,Fe)$_9$S$_8$/NIF(Fe:50%).

Figure S19. Polarization curves with iR-corrected of N-Ni$_3$S$_2$/NF, N-(Ni,Fe)$_3$S$_2$/NIF(Fe:15%) and N-(Ni,Fe)$_9$S$_8$/NIF(Fe:50%) in 1M KOH solution at a scan rate of 1 mV s$^{-1}$ and 25 °C.
Figure S20. XRD pattern of N-(Ni,Fe)$_3$S$_2$/NIF after OER.
Figure S21. EDX elemental mapping images of N-(Ni,Fe)$_2$S$_2$ after OER.