Supplementary Information

Mo-triggered Amorphous Ni$_3$S$_2$ Nanosheets as Efficient and Durable Electrocatalysts for Water Splitting

Haoxuan Zhang, Hao Jiang,* Yanjie Hu, Petr Saha, Chunzhong Li*# 

a. Key Laboratory for Ultrafine Materials of Ministry of Education & School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China

b. Centre of Polymer Systems, University Institute, Tomas Bata University in Zlin, Trida T. Bati 5678, 760 01 Zlin, Czech Republic

Email: jianghao@ecust.edu.cn (Prof. H. Jiang) and czli@ecust.edu.cn (Prof. C. Z. Li)
Part I: Experimental Section

1.1 Synthesis of α-Mo-Ni$_3$S$_2$ nanosheets:

Prior to use, commercial Ni foam (0.6 cm × 0.5 cm × 0.3 mm) was immersed in 3 M HCl for 20 minutes to remove surface oxide layer. In a typical synthesis, 8 mmol of CH$_3$CSNH$_2$ and 2 mmol of Na$_2$MoO$_4$ were grinded in a mortar for 10 minutes. The mixture was then put into a 5 mL flask. Subsequently, a piece of cleaned Ni foam was embedded in the mixture at 220 °C for 40 minutes. After cooled down to room temperature, washed with distilled water, absolute ethanol and carbon disulfide for several times, the resulting products have been obtained. The Mo content in products can be easily controlled by changing the amount of Na$_2$MoO$_4$, e.g. 6.3 % (0.5 mmol), 7.4 % (1.0 mmol), 11.5 % (1.5 mmol), 12.5 % (2.0 mmol) and 16.7 (2.5 mmol). Without the addition of Na$_2$MoO$_4$, the crystalline Ni$_3$S$_2$ products have been obtained.

1.2 Characterization:

Scanning electron microscopy (SEM) images were taken from a Hitachi, S-4800 FE-SEM at an accelerating voltage of 15.0 kV. Transmission electron microscopy (TEM) and high-resolution transmission (HR-TEM) images were taken from a JEOL, JEM-2100F TEM with an X-ray Energy-dispersive spectrometer (EDS) at an accelerating voltage of 200.0 kV. X-ray powder diffraction (XRD) patterns were recorded on a Rigaku D/Max 2550 diffractometer with Cu Kα radiation at a scan rate of 1° min$^{-1}$. X-ray photoelectron spectroscopy (XPS) spectra were recorded on an ESCALAB 250Xi X-ray photoelectron spectrometer at a pass energy of 40 eV with an Al Kα X-ray source. Inductively coupled plasma mass spectrometry (ICP-MS) was performed
by an Agilent 7700 spectrometer. The samples were directly conducted by X-ray
diffraction and scanning electron microscopy, and were dispersed in absolute ethanol
for 10-min ultrasound bath before transmission electron microscopy, and were grinded
to powder for X-ray photoelectron spectra and inductively coupled plasma mass
spectrometry.

1.3 Electrochemical Measurements:

The electrochemical measurements for HER and OER were performed in a standard
three-electrode system controlled by a CHI660E electrochemical workstation (Chenhua,
Shanghai) with saturated Ag/AgCl and graphite electrode as reference electrode and
counter electrode, respectively. The electrocatalysts supported on Ni foam were directly
used as working electrode. All measurements were carried out in 1.0 M KOH aqueous
solution under gently stirring to remove bubbles. The measured potentials were calibrated to
reversible hydrogen electrode (RHE) by the following equation:

\[ E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.1976 + 0.0591 \times pH \]

Before HER and OER tests, the electrolyte was purged with N\(_2\) and O\(_2\) for at least 30 minutes
to achieve an N\(_2\) and O\(_2\)-saturated condition, respectively. After that, the electrocatalysts were
activated at a constant current density of 10 mA cm\(^{-2}\) until attaining stable potentials. The
LSV curves were recorded at a scan rate of 1 mV s\(^{-1}\). The chronopotentiometry was
performed under the same condition. The electrochemical data was presented with 95% \(iR\)
drop compensation. The solution resistance (R) was calculated based on the electrochemical
impedance spectroscopy (EIS) results measured at -0.15 V vs. RHE for HER and 1.53 V vs. RHE for OER in frequencies range from 10 kHz to 100 mHz. The resistance value is equal to
the total impedance at the phase angle of $0^\circ$ in high frequency. The turnover frequency (TOF) was calculated by the following equation:

$$TOF = \frac{J \times A}{2 \times F \times n}$$

where $J$ is the current density in the LSV curves, $A$ is the geometric area of electrode, $F$ is the Faraday constant (C mol$^{-1}$), and $n$ is the mole number of active sites on the electrode.
Part II: Supporting Figures

**Fig. S1** Digital photograph of pristine Ni foam and the a-Mo-Ni$_3$S$_2$ nanosheets.

**Fig. S2** (a) SEM image and (b) XRD pattern of the c-Ni$_3$S$_2$ products.

**Fig. S3** SEM image of the a-Mo-Ni$_3$S$_2$ nanosheets.
**Fig. S4** TEM image of the a-Mo-Ni$_3$S$_2$ nanosheets.

**Fig. S5** Cyclic voltammograms curves of (a) the a-Mo-Ni$_3$S$_2$ and (b) the c-Ni$_3$S$_2$ electrocatalysts with pristine Ni foam as a control in pH = 7 at a scan rate of 50 mV s$^{-1}$.

**Fig. S6** XRD pattern of the a-Mo-Ni$_3$S$_2$ electrocatalysts after HER.
**Fig. S7** Cyclic voltammograms curves of (a) the a-Mo-Ni$_3$S$_2$ and (b) the c-Ni$_3$S$_2$ electrocatalysts in the non-faradic potential range of 0.9 - 1.0 V at different scan rates.

**Fig. S8** The charging currents measured at 0.95 V vs. RHE plotted as a function of scan rate. The double-layer capacitance of the a-Mo-Ni$_3$S$_2$ and the c-Ni$_3$S$_2$ electrocatalysts is obtained from the slope of the linear fits to the data.
**Fig. S9** Mo 3d XPS spectra of the a-Mo-Ni$_3$S$_2$ and the c-Ni$_3$S$_2$ electrocatalysts after HER.

**Fig. S10** Ni 2p$_{3/2}$ XPS spectra of the Mo-Ni$_3$S$_2$ products with different Mo content after HER.

**Fig. S11** HER polarization curves of the Mo-doped Ni$_3$S$_2$ products with different Mo content.
**Fig. S12** (a) Tafel plots of the a-Mo-Ni$_3$S$_2$, the c-Ni$_3$S$_2$, the commercial IrO$_2$ and RuO$_2$ electrocatalysts, (b) the calculated exchange current density of the a-Mo-Ni$_3$S$_2$ and c-Ni$_3$S$_2$ electrocatalysts for OER. Such excellent OER performances of a-Mo-Ni$_3$S$_2$ catalysts surpass other reported electrocatalysts to date. For instance, Zou et al. reported amorphous Ni-Fe bimetallic hydroxide film-coated, nickel foam-supported, Ni$_3$S$_2$ nanosheet arrays by a facile ultrafast synthetic approach, which required a higher overpotential of 320 mV to obtain 100 mA cm$^{-2}$.$^1$

**Fig. S13** Chronopotentiometry curve of the a-Mo-Ni$_3$S$_2$ electrocatalysts for OER.
Fig. S14 (a) SEM image and (b) XRD pattern of the a-Mo-Ni₃S₂ electrocatalysts after OER.

Fig. S15 XPS spectra of (a) Ni 2p₃/₂, (b) O 1s, (c) Mo 3d and (d) S 2p regions of the a-Mo-Ni₃S₂ and the c-Ni₃S₂ electrocatalysts after OER. For Ni 2p₃/₂ region, the peak at 857.2 eV in the a-Mo-Ni₃S₂ samples indicates the Ni³⁺ generation during OER. The Ni³⁺ content is 15 % by integrating the respective peak areas, nearly four times higher than the c-Ni₃S₂. For O 1s region, the peak of OOH* intermediates appears at 529.1 eV in the a-Mo-Ni₃S₂ with the content of 10 %, which is two times higher than the c-Ni₃S₂.
### Part III: Supporting Table

**Tab. S1** The comparisons of HER performance of various Ni-based electrocatalysts.

<table>
<thead>
<tr>
<th>Electrocatalyst</th>
<th>Measurement</th>
<th>J (mA cm⁻²)</th>
<th>η (mV)</th>
<th>Tafel slope (mV dec⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu@CoSₓ</td>
<td>Cu foam, 1.0 M KOH</td>
<td>10</td>
<td>134</td>
<td>61</td>
<td>8</td>
</tr>
<tr>
<td>MoOₓ/NiₓSᵧ microsphere</td>
<td>Ni foam, 1.0 M KOH</td>
<td>10</td>
<td>106</td>
<td>90</td>
<td>11</td>
</tr>
<tr>
<td>NiₓSᵧ nanosheet arrays</td>
<td>Ni foam, 1.0 M KOH</td>
<td>10</td>
<td>223</td>
<td>/</td>
<td>12</td>
</tr>
<tr>
<td>N doped NiₓSᵧ nanosheets</td>
<td>Ni foam, 1.0 M KOH</td>
<td>10</td>
<td>155</td>
<td>113</td>
<td>S2</td>
</tr>
<tr>
<td>Cu decorated NiₓSᵧ nanotubes</td>
<td>Carbon fiber, 1.0 M KOH</td>
<td>10</td>
<td>128</td>
<td>76</td>
<td>S3</td>
</tr>
<tr>
<td>Ni(OH)ₓ@CuS</td>
<td>Glass carbon, 1.0 M KOH</td>
<td>10</td>
<td>95</td>
<td>104</td>
<td>S4</td>
</tr>
<tr>
<td>NiCu@C</td>
<td>Graphite plate, 1.0 M KOH</td>
<td>10</td>
<td>74</td>
<td>94</td>
<td>S5</td>
</tr>
<tr>
<td>MoSᵧ-NiₓSᵧ heteronanorods</td>
<td>Ni foam, 1.0 M KOH</td>
<td>10</td>
<td>98</td>
<td>61</td>
<td>S6</td>
</tr>
<tr>
<td>NiₓCoₓ₋ₓSᵧ/NiₓSᵧ nanosheet arrays</td>
<td>Ni foam, 1.0 M KOH</td>
<td>10</td>
<td>136</td>
<td>107</td>
<td>S7</td>
</tr>
<tr>
<td>Ni(OH)ₓ nanosheets</td>
<td>Carbon cloth, 1.0 M KOH</td>
<td>10</td>
<td>80</td>
<td>70</td>
<td>S8</td>
</tr>
<tr>
<td>Fe-doped NiₓSᵧ nanosheets</td>
<td>Ni foam, 1.0 M KOH</td>
<td>50</td>
<td>214</td>
<td>/</td>
<td>S9</td>
</tr>
<tr>
<td>V-doped NiₓSᵧ nanosheets</td>
<td>Glass carbon, 1.0 M KOH</td>
<td>10</td>
<td>110</td>
<td>90</td>
<td>S10</td>
</tr>
<tr>
<td>N decorated NiₓSᵧ</td>
<td>Ni foam, 1.0 M KOH</td>
<td>10</td>
<td>110</td>
<td>70</td>
<td>S11</td>
</tr>
<tr>
<td>Ni/NiP</td>
<td>Ni foam, 1.0 M KOH</td>
<td>10</td>
<td>130</td>
<td>58</td>
<td>S12</td>
</tr>
<tr>
<td>Porous NiₓP</td>
<td>Ni foam, 1.0 M KOH</td>
<td>10</td>
<td>98</td>
<td>72</td>
<td>S13</td>
</tr>
<tr>
<td>MoSᵧ-NiₓSᵧ heterostructures</td>
<td>Ni foam, 1.0 M KOH</td>
<td>10</td>
<td>110</td>
<td>83</td>
<td>S14</td>
</tr>
<tr>
<td>Ni-P nanosheets</td>
<td>Carbon cloth, 1.0 M KOH</td>
<td>10</td>
<td>98</td>
<td>59</td>
<td>S15</td>
</tr>
<tr>
<td><strong>This work</strong></td>
<td>Ni foam, 1.0 M KOH</td>
<td>10</td>
<td>74</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>134</td>
<td>54</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
References


Mater. 2016, 26, 3314.

