Supporting Information

Construction of Amorphous Interface in NiS/NiS$_2$ Interwoven Structure for Enhanced Overall Water Splitting

Qun Li,$^{a,b}$ Dewen Wang,$^{a,b}$ Ce Han,$^a$ Xiao Ma,$^{a,c}$ Qingqing Lu,$^{a,c}$ Zhicai Xing$^a$ and Xiurong Yang$^{a,*}$

$^a$State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, Jilin, China

$^b$University of Science and Technology of China, Hefei 230026, China

$^c$University of Chinese Academy of Sciences, Beijing 100049, China

*Corresponding Author: Tel: +86-431-85262056; E-mail: xryang@ciac.ac.cn

Experimental details

Materials

All chemicals were used as received without any purification. Nickel sulfate hexahydrate (NiSO$_4$·6H$_2$O) was purchased from Tianjin Fuchen Chemical Reagent Co. Inc., China. Carbon cloth (CC) was provided by CeTech Co. Ltd, China. Thiourea (CH$_4$N$_2$S), Pt/C (10 wt %) and Ruthenium (IV) oxide (RuO$_2$) were purchased from Sigma-Aldrich. Deionized water (DIW, 18.25 MΩ cm) was used throughout the experiment.

Synthesis of NiS$_x$

NiSO$_4$·6H$_2$O (0.26 g) and CH$_4$N$_2$S (0.26 g) were firstly ground into small particles by a mortar. The NiS$_x$ were successfully synthesized by a one step thermal sulfidation of the mixture at 400, 450, or 500 °C for 2 h under Ar atmosphere in a horizontal tube furnace.
Preparation of electrodes

20 mg of NiS\textsubscript{x} was ultrasonically dispersed into 0.5 mL DIW, 0.495 mL ethanol, and 0.05 mL of 5 wt% Nafion® solution and then the ink was transferred onto CC electrode \textit{via} a controlled drop casting method, with a loading amount of 2.4 mg cm\textsuperscript{-2}. The 10% Pt/C and RuO\textsubscript{2} electrodes also prepared as NiS\textsubscript{x} electrodes with the same loading of approximately 2.4 mg cm\textsuperscript{-2}.

Physical methods

The X-ray diffraction (XRD) patterns were measured on a D8 ADVANCE diffractometer (Bruker, Germany) using Cu-K \textalpha{} radiation (λ = 1.54 Å). The morphologies were observed under scanning electron microscopy (SEM) (OXFORD Instrument XMAX) with an accelerating voltage of 20 kV. The transmission electron microscopy (TEM) images were conducted on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) operating at 200 kV. X-ray photoelectron spectroscopy (XPS) data were collected by an ESCALABMK II X-ray photoelectron spectrometer equipped with an Mg K\textalpha{} source. X-ray absorption near edge structure (XANES) spectroscopy were performed on the 1W2B end station, Beijing Synchrotron Radiation Facility (BSRF). The Ni K-edge spectra were measured in the transmission mode under room temperature. The content of dissolved S in solution during long-term stability testing for HER and OER were measured by inductively coupled plasma optical emission spectrometry (ICP-OES, Thermo ICAP 6300). Raman characterization was carried out on a Renishaw 2000 model confocal microscopy Raman spectrometer with an air-cooled charge coupled device and a holographic notch filter (Renishaw Ltd., U.K.). The Brunauer-Emmett-Teller (BET) surface area and pore size were calculated from N\textsubscript{2} adsorption–desorption isotherms measured at 77 K on an Autosorb iQ Station.
Electrochemical measurements

Electrochemical performances were tested in a typical three-electrode setup using a CHI660 potentiostat (CH Instruments, China) in 1.0 M KOH. The graphite rod and Hg/HgO were used as counter electrode and reference electrode, respectively. Linear sweep voltammetry measurements (LSVs) were conducted from -0.8 to -1.6 V for HER at a scan rate of 2 mV s\(^{-1}\) and 0 to 1 V for OER at a scan rate of 5 mV s\(^{-1}\). Cyclic voltammetries (CVs) were conducted from -0.8 to -1.26 V for HER and 0 to 1 V for OER at 100 mV s\(^{-1}\). Long-term stability testing was conducted with chronoamperometry under selected voltage. Considering the effect of ohmic resistance on intrinsic catalytic activity, all the electrochemical data are presented with \(iR\) compensation (except for water splitting) for further analysis. The current densities were normalized to the geometrical surface area and the measured potentials are converted to a reversible hydrogen electrode (RHE) scale (the Hg/HgO reference electrode was calibrated in H\(_2\) saturated 1.0 M KOH with Pt wire as work electrode and counter electrode). The overpotential is calculated as follows: 

\[
\eta_{HER} = E_{RHE}; \\
\eta_{OER} = E_{RHE} - 1.23V.
\]

Measurements of electrochemical impedance spectroscopy (EIS)

EIS were performed under open circuit potentials for all materials and the frequency range from 100 kHz to 0.1 Hz were applied to carry out the measurements. The impedance data were represented by Nyquist plots, which were fitted using Autolab software, Nova 1.8. At high frequency, the intersection with the \(Z'\) axis (real impedance axis) represents the intrinsic Ohmic resistance of the internal resistance or equivalent series resistance of the electrode material and electrolyte, which is described as \(R_S\) and employed for series resistance compensation.
Faradaic efficiency measurements

The quantitative measurements of faradaic H$_2$ and O$_2$ yield were performed in an H-type electrolytic cell. The H$_2$ or O$_2$ was produced by a constant current of 0.25 A on an electrode with a projected area of 4 cm$^2$ (2 cm × 2 cm). The volume of H$_2$ or O$_2$ was collected by a water drainage method. The theoretical volume of H$_2$ or O$_2$ was calculated by applying the ideal gas law and the Faraday law.

Figures and Tables

**Fig. S1.** Cartoon showing the structural difference between the core-shell structure and the interwoven structure.
Fig. S2. Schematic of the synthetic process and optical photographic images for NiS$_x$.

Fig. S3. The XPS spectra for (A) Ni 2p and (B) S 2p in NiS and NiS$_2$. 
Table 1. EXAFS fitting results deduced from Ni K-edge spectra of NiS/NiS$_2$.

<table>
<thead>
<tr>
<th>shells</th>
<th>CN</th>
<th>R(Å)</th>
<th>$\sigma^2$(Å$^2$)</th>
<th>$\Delta E$</th>
<th>R-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiS/NiS$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-S</td>
<td>6.3±0.2</td>
<td>2.39±0.01</td>
<td>0.0078±0.0003</td>
<td>1.3±0.3</td>
<td>0.00055</td>
</tr>
<tr>
<td>Ni-Ni</td>
<td>0.2±0.1</td>
<td>2.73±0.03</td>
<td>0.0069±0.0011</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-S</td>
<td>3.7±0.3</td>
<td>3.54±0.01</td>
<td>0.0078±0.0003</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-Ni</td>
<td>3.9±0.6</td>
<td>4.02±0.01</td>
<td>0.0069±0.0011</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

CN: coordination number, R(Å): inter-atomic distance, $\sigma^2$: mean-square relative displacement (Debye Waller factor), $\Delta E$: shift of $E_0$ value, R-factor is a measure of the misfit distribution over both data sets (%).

Table 2. The Ni-S and Ni–Ni distances for NiS, NiS$_2$ and NiS/NiS$_2$.

<table>
<thead>
<tr>
<th></th>
<th>Ni-S</th>
<th>Ni-Ni</th>
<th>Ni-Ni</th>
<th>Ni-S</th>
<th>Ni-Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiS</td>
<td>2.378</td>
<td>2.650</td>
<td>3.420</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NiS$_2$</td>
<td>2.401</td>
<td>-</td>
<td>-</td>
<td>3.539</td>
<td>4.021</td>
</tr>
<tr>
<td>NiS/NiS$_2$</td>
<td>2.39</td>
<td>2.73</td>
<td>-</td>
<td>3.54</td>
<td>4.02</td>
</tr>
</tbody>
</table>

Fig. S4. The crystal structure for (A) NiS and (B) NiS$_2$. 

S6
**Fig. S5.** TEM images for (A) NiS$_2$ and (B) NiS.

**Fig. S6.** HRTEM images for NiS/NiS$_2$. 
Fig. S7. HRTEM images for (A) NiS$_2$ and (B) NiS.

Fig. S8. Nyquist plots of electrochemical impedance spectra of different materials under open circuit potentials.
**Fig. S9.** (A) Tafel plots for NiS$_x$ and Pt/C, (B) Time-dependent current density curve for NiS/NiS$_2$ under static $\eta$ of 156 mV for HER.

**Fig. S10.** (A) Tafel plots for NiS$_x$ and RuO$_2$. (B) Time-dependent current density curve for NiS/NiS$_2$ under static 358 mV for OER.
Fig. S11. Electrocatalytic efficiency of NiS/NiS$_2$ for (A) HER and (B) OER.

Fig. S12. (A) The amount of S species in the electrolyte for HER and OER (electrode area: 0.5 cm $\times$ 0.5 cm) with constant current density of 50 mA cm$^{-2}$. (B) Raman spectra for NiS/NiS$_2$ before and after 12 h electrolysis for OER (the peaks appear at $\sim$274 and $\sim$560 cm$^{-1}$ derived from NiS$_2$ and NiOOH, respectively; the peak around 478 cm$^{-1}$ can be assigned to both NiS$_2$ and NiOOH) (J. Phys. Chem. C, 2012, 116, 8394–8400; J. Phys. Chem. C, 2013, 117, 6561–6566; Catal. Sci. Technol., 2017, 7, 3591–3597).
Fig. S13. XRD patterns of NiS/NiS₂ before and after 24 h electrolysis.

Fig. S14. Polarization curve and corresponding Tafel plot of NiS-NiS₂ for (A, B) HER and (C, D) OER.
Fig. S15. Enlargement of the Ni oxidation range in LSV curves of Fig. 3C. The ratio of the number of active sites for NiS/NiS$_2$, NiS$_2$ and NiS is 2.9: 1.6: 1 which calculated from the area integral of oxidation peak.

Fig. S16. (A) Nitrogen adsorption/desorption isotherm and (B) the BJH pore-size distribution curves for NiS$_x$. The surface areas are 154.0, 173.5 and 247.5 m$^2$ g$^{-1}$ for NiS$_2$, NiS/NiS$_2$ and NiS, respectively. In addition, the pore sizes for NiS$_x$ is mainly concentrated around 3.6-3.8 nm.