Experimental Section

A typical synthetic process is as follows: 30.0 mg thioacetamide (Sigma-Aldrich) was dissolved in 5.0 mL of deionized water and then 1.5 mL of N₂H₄·H₂O (35 wt% solutions in water, Sigma-Aldrich) was added to the above solution under vigorously stirring. After 5.0 min, 47.5 mg NiCl₂·6H₂O (Chem-Supply) was added to the above mixture with stirring for 10 min. The resulting solution was transferred into a Teflon-lined stainless steel autoclave with a volume of 20.0 mL. Subsequently, a piece of pre-treated FTO conducting glass (15
Ω/square, Nippon Sheet Glass, Japan) with conductive facing up was put into the above reaction solution with an angle of 45°. The hydrothermal reaction was performed at different temperatures (120, 150 and 180 °C) for 24 h to study the temperature effect on the resulting NiS structure and electrocatalytic activity (denoted as NiS-X-24h, where X is reaction temperature). For the time-dependent experiments, the hydrothermal reaction was performed at 180 °C for different reaction times (6 h, 12 h and 24 h, denoted as NiS-180-N, where N is reaction time). After hydrothermal reaction, the autoclave was cooled to room temperature and then FTO substrate was taken out, rinsed adequately with deionized water and allowed to dry in an ambient atmosphere. The resulting NiS nanostructured films were further characterised and tested in DSSCs.

Characterisation

TEM (Philips F20), SEM (JSM-6300F) and XRD (Shimadzu XRD-6000 diffractometer) were employed for characterizing the prepared samples. Chemical compositions of the samples were analysed by X-ray photoelectron spectroscopy (XPS, Kratos Axis ULTRA incorporating a 165 mm hemispherical electron energy analyzer). Photoluminescence spectra (Hitachi F-7000, excitation wavelength: 370 nm, scanning rate: 1200 nm min⁻¹, PMT voltage: 800 V, widths of the excitation slit and emission slit: 10.0 nm) was tested by dispersing the obtained powder (scraped from FTO) into distilled water after 30 min sonication.

Measurements

A series of DSSCs were fabricated with traditional sandwich type configuration by using a dye-anchored TiO₂ photoelectrode (Dyesol, Australia) which was pre-calcinated at 450 °C for 0.5 h before dye loading. The dye-anchored TiO₂ photoanode (0.25 cm²) and NiS nanostructured film counter electrode were assembled into a sandwich type cell and sealed with a hot-melt gasket of the ionomer Surlyn 1702 (Dyesol, Australia). More details of the DSSCs assembly can be found in reference.¹ For a meaningful comparison, a commercially
available Pt counter electrode (Dyesol, Australia) was also tested for DSSCs using a similar assembly approach described as above. Cyclic voltammetry (CV) was tested in an acetonitrile solution containing 1.0 mM I$_2$, 10.0 mM LiI and 0.1 M LiClO$_4$ in a three-electrode system at a scan rate of 50 mV s$^{-1}$ with a computer-controlled potentiostat (Princeton Applied Research, Parstat 2273). For all investigated samples, the CV curves exhibit two pairs of oxidation and reduction peaks in the range of -0.6 to 1.2 V (vs. Ag/AgCl). A 500 W Xe lamp (Trusttech Co., Beijing) with an AM 1.5G filter (Sciencetech, Canada) was used as the light source. The light intensity was measured by a radiant power meter (Newport, 70260) coupled with a broadband probe (Newport, 70268). The photovoltaic measurements of DSSCs were recorded by a scanning potentiostat (Model 362, Princeton Applied Research, US). Impedance measurements were performed with a computer-controlled potentiostat (Princeton Applied Research, Parstat 2273) using symmetric cells fabricated with two identical electrodes. The frequency range is 0.1 Hz to 1 M Hz and the magnitude of the modulation signal is 10 mV.$^2$

Tafel polarization curves were obtained using symmetrical cells, at a scanning rate of 10 mV/s, using a CHI 760D with a two-electrode system the same as impedance measurement.$^2$

**Theoretical Calculations**

All the spin-polarised calculations were performed with Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation using the Vienna ab-initio simulation package (VASP) code. The project-augmented wave (PAW) method was used to represent the core-valence electron interaction. The valence electronic states were expanded in plane wave basis sets with energy cutoff at 450 eV. The occupancy of the one-electron states was calculated using the Gaussian smearing (SIGMA=0.05 eV) for the NiS (0001) surface. The ionic degrees of freedom were relaxed using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) minimization scheme until the Hellman-Feynman forces on each ion were less than 0.05 eV/Å. The dipole correction was performed throughout the calculations to take
the polarisation effect into account. As for model construction, considering that iodine molecule bond is up to 2.68 Å, a large $p(4 \times 4)$ NiS (0001) slab was built to minimise the lateral interaction between adjacent I atoms. The vacuum between slabs is ~20 Å, and a corresponding 1×1×1 k-points mesh was used during optimisations. To check the polarisation effect for the polar NiS (0001) surface, we tested different atomic layers and got similar I adsorption energies of -0.62 eV, -0.58 eV and -0.66 eV for five-, nine- and thirteen layer, respectively.

The adsorption energy of I ($E_{ad}^I$) is defined as:

$$E_{ad}^I = E(I/sur) - E(sur) - 1/2E(I_2)$$

where $E(sur)$, $E(I_2)$ and $E(I/sur)$ are the energies of the catalyst surface, $I_2$ in the gas phase and I adsorbed on the catalyst surface, respectively. The more negative $E_{ad}^I$ is, the more strongly the species I bind on surface.
Table S1 Photovoltaic parameters of DSSCs with different counter electrodes.

<table>
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<tr>
<th>Electrodes</th>
<th>$J_{sc}$ [mA cm$^{-2}$]</th>
<th>$V_{oc}$ [mV]</th>
<th>$FF$ [%]</th>
<th>$LCE$ [%]</th>
<th>$R_{ct}$ [Ω]</th>
<th>$R_s$ [Ω]</th>
<th>$Z_w$ [Ω]</th>
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<tr>
<td>Pt</td>
<td>15.21</td>
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<td>NiS-120-24h</td>
<td>15.53</td>
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<td>5.52</td>
<td>12.42</td>
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<tr>
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<td>695</td>
<td>61.2</td>
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<td>7.23</td>
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<tr>
<td>NiS-180-6h</td>
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<td>713</td>
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<tr>
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<td>62.7</td>
<td>8.62</td>
<td>2.22</td>
<td>19.25</td>
<td>0.92</td>
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</tbody>
</table>
Fig. S1 XRD patterns of the as-synthesised NiS samples at different temperatures for 24 h.
Fig. S2 (a) XPS survey spectra of NiS samples synthesised at different temperatures for 24 h. (b) and (c) High resolution XPS spectra of S and Ni.
Fig. S3 SEM images of the as-synthesised NiS samples (a) 120 °C for 24 h. (b) 150 °C for 24 h.
Fig. S4 SEM images of the as-synthesised NiS samples with different reaction time at 180 °C. (a) 6 h. (b) 12 h.
Fig. S5 Nyquist plots of symmetric dummy cells with Pt and NiS counter electrodes.
Fig. S6 Tafel polarisation curves of symmetric dummy cells with Pt and NiS counter electrodes.
**Fig. S7** Photoluminescence spectrum of the as-prepared NiS nanosheet sample measured at room temperature at an excitation wavelength of 370 nm (inset).

**References**
