

**Electronic Supplementary Information (ESI) for**  
**NiSe<sub>2</sub> as an efficient electrocatalyst for Pt-free counter electrode of**  
**dye-sensitized solar cell**

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## **Experimental**

### **Synthesis of NiSe<sub>2</sub>**

The NiSe<sub>2</sub> product was synthesized *via* a one-step hydrothermal reaction.<sup>1</sup> Firstly, 0.32 g Se powder (99.999%, Aladdin) was dissolved in 30 ml of NaOH (4 g, Sinopharm) aqueous solution (solution A). Solution B was prepared from 0.48 g NiCl<sub>2</sub>·6H<sub>2</sub>O (99.9%, Alfa Aesar) and 0.93 g EDTA-2Na (>99%, J&K) dissolved in 30 ml deionized water. The two solutions were then added to a 100 mL Teflon-lined autoclave with vigorous stirring for 10 min. The autoclave was maintained at 200 °C for 6 h, and then cooled down to room temperature naturally. A large amount of black precipitate was collected and washed several times, and dried in vacuum at 60 °C for 24 h.

### **Characterizations**

XRD pattern of the obtained selenide was recorded on an X-ray powder diffractometer (D8 Advance, Bruker) with Cu K<sub>α</sub> radiation ( $\lambda = 0.154$  nm). The composition of the synthesized selenide was confirmed by inductive coupling plasma-atomic emission spectrometer (ICP-AES, Thermo Electron Corporation Adv.

ER/S). The Brunauer-Emmett-Teller (BET) specific surface area for the hydrothermal product was analyzed by the BET equation using a surface area and porosity analyzer (ASAP 2020, Micromeritics). The morphology of the NiSe<sub>2</sub> powder was examined by FESEM (S-4800, Hitachi). Cyclic voltammetry (CV) was carried out in a three-electrode system containing an anhydrous acetonitrile solution of 0.1 M LiClO<sub>4</sub>, 10 mM LiI, and 1 mM I<sub>2</sub> at a scan rate of 50 mV s<sup>-1</sup>, using a platinum wire as the counter electrode, an Ag/Ag<sup>+</sup> electrode as the reference electrode and the prepared CEs as working electrodes. For electrochemical impedance spectroscopy (EIS) and Tafel polarization measurements, the symmetrical cells were assembled with two identical CEs filled with the same electrolyte as used in DSSCs. In EIS tests, the samples were measured from 0.1 Hz to 500 kHz at 0 V bias and ac amplitude of 10 mV. The polarization measurements were performed at a scan rate of 50 mV s<sup>-1</sup>. All the electrochemical characterizations were performed on an electrochemical workstation (ZAHNER ZENNIUM CIMPS-1, Germany). The photocurrent density-voltage curves of DSSCs were recorded on a Keithley 2400 source meter under the illumination of AM1.5G simulated solar light coming from an AAA solar simulator (Newport-94043A) equipped with a Xe lamp (450 W) and an AM1.5G filter. The light intensity was calibrated using a reference Si solar cell (Oriel-91150). A black mask with an aperture area of 0.2304 cm<sup>2</sup> was applied on the surface of DSSCs to avoid stray light completely.

### **Fabrication of CEs and DSSCs**

The reference Pt CE used in this research was prepared by deposition of 50 μL H<sub>2</sub>PtCl<sub>6</sub> ethanol solution (3 mM) on an 1.5×1.5 cm<sup>2</sup> FTO glass followed by 400 °C heat treatment for 30 min.<sup>2</sup> We had tested that the Pt loading amount of the Pt CE (23 μg cm<sup>-2</sup>) and the BET surface area of pyrolytic Pt (5.8 m<sup>2</sup> g<sup>-1</sup>). For the hot-pressed surlyn spacer in DSSCs with an exposed area of 0.36 cm<sup>2</sup>, the active surface area of Pt CE was estimated to be 0.480 cm<sup>2</sup>.

For directly comparing the catalytic activity of NiSe<sub>2</sub> with Pt, we should control the

loading amount of NiSe<sub>2</sub> with the same active surface area as that of the Pt CE. Firstly, we measured the BET surface area for the as-prepared NiSe<sub>2</sub> in advance, which is approximately 2.2 m<sup>2</sup> g<sup>-1</sup>. And then, we drop-casted 50 μL NiSe<sub>2</sub> suspension (0.44 mg mL<sup>-1</sup>) onto the surface of FTO glass, which was masked by a 3M scotch tape with an exposed area of 0.6×0.6 cm<sup>2</sup>. In this way, the active surface area (0.484 cm<sup>2</sup>) of NiSe<sub>2</sub> catalyst deposited on FTO glass was approximately equal with that for the Pt CE (0.480 cm<sup>2</sup>).

12-μm-thick TiO<sub>2</sub> photoanodes were prepared according to a previous paper,<sup>3</sup> which were soaked overnight in the N719 solution (Lumtec Corp., 0.3 mM in a mixed solvent of acetonitrile and tert-butanol by a volume ratio of 1:1). The DSSCs were assembled with a photoanode, a CE, and an electrolyte containing 0.1 M LiI, 0.05 M I<sub>2</sub>, 0.6 M 1,2-dimethyl-3-n-propylimidazolium iodide (Sigma-Aldrich Co.) and 0.5 M 4-*tert*-butylpyridine (Acros) in dry acetonitrile.

## References

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