Supplementary Information for
Oriented single crystalline nickel sulfide nanorod arrays: “two-in-one” counter electrodes for dye-sensitized solar cells

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Experimental procedure for NiS NRAs on bare glass substrate

All reactants were analytically pure, and used as received. Bare and conductive glass substrates were cleaned by sonication in a diluted HCl aqueous solution, acetone, distilled water, and ethanol for 10 min each. To grow single-crystalline NiS NRAs, the precursor solution was prepared by dissolving 5 mmol NiSO₄·7H₂O and 5 mmol thiourea in 10 mL distilled water, followed by addition of 10 mL condensed aqueous ammonia (25-28%). After stirring for 60 min, the mixture solution was transferred into a Teflon-lined steel autoclave with a capacity of 50 mL. A piece of cleaned substrate was placed at an angle against the wall of the Teflon-liner, and kept at 150 °C. The autoclave was sealed, maintained at 150 °C for 5, 10, 20 h, and cooled to room temperature naturally. The as-fabricated NiS NRAs were sequentially denoted as G-NiS5, G-NiS10 and G-NiS20.

TiO₂ photoanode preparation and cells fabrication

Firstly, 12 µm thick transparent films of 20 nm-sized TiO₂ particles were screen printed on the FTO substrates. The electrodes were sintered in dry air at 450 °C for 30 min. Subsequently, the electrodes were immersed in 40 mM of TiCl₄ aqueous solution at 70 °C for 30 min. After sintered in dry air at 450 °C for 30 min again, the electrodes were immersed into a 0.3 mM solution of ruthenium dye N719 in anhydrous ethanol overnight. Furthermore, Pt sputtered onto FTO and NiS NRA films were used as counter electrodes. The electrolyte used consisted of 0.1 M LiI, 0.05 M I₂, 0.3 M 1,2-dimethyl-3-propylimidazolium iodine, and 0.5 M tert-butylpyridine in 3-methoxypropionitrile. Finally, the photoanode and the counter electrode were
assembled and clipped in a sandwich type arrangement with the electrolyte solution placed in between. The active area was 0.25 cm$^2$. The symmetric cell configuration with an effective area of 1 cm$^2$ for EIS spectra assembled with two identical CEs sandwiching the electrolyte.

Density functional theory (DFT) calculations.

All computations were implemented within the framework of density functional theory (DFT) and the HSE06 hybrid function was used to describe the exchange correlation functional. The cutoff energy of plane wave was chosen at 400 eV. For the BZ integration, we used $4 \times 4 \times 4 \Gamma$-centered Monkhorst–Pack grids. The relaxation and optimization of configurations were performed until the total energy changes fell below $10^{-5}$ eV/atom and the Hellmann–Feynman force on all atomic sites was less than 0.01 eV/Å.

Characterization and electrochemical measurements

X-ray diffraction (XRD) measurement was performed with a D8 Brueker diffractometer in the 20 range of 10-80°. SEM images and EDS analysis were taken on a JEOL JSM-6400F microscope equipped with an EDS analytical system. High resolution transmission electron microscope (HRTEM) images and SAED patterns were carried out with a JEOL JEM-2100F transmission electron microscope operated at 200 kV. Photocurrent density–voltage characteristics were measured using a Keithley Model 2440 source meter under AM 1.5 illumination. A 1000 W Oriel solar simulator was used as a light source and the power of the light was calibrated to one sun light intensity by using a NREL-calibrated Si cell (Oriel 91150). Cyclic
voltammetry (CV) were performed with a CHI660B electrochemical workstation in a three-electrode setup, which consisted of the FTO-Pt or NiS NRA working electrode, a platinum foil counter electrode, and a Ag/AgCl reference electrode. The scan rate is 50 mVs\(^{-1}\). The electrolyte for measurement was acetonitrile solution containing 0.1 M LiClO\(_4\), 10 mM LiI, 1 mM I\(_2\). The electrochemical impedance spectroscopy (EIS) measurements were performed in the dark with a computer-controlled potentiostat (Solartron 1287, UK) by applying an AC voltage with 10 mV amplitude in a frequency range from 0.01 Hz to 100 kHz. The spectra were fitted by Zview software.
Figure S1. XRD patterns of as-prepared NiS NRAs with increased reaction time.

All the patterns can be indexed to millerite NiS without impurity phase. But the peak intensities increased with extended reaction time, indicating the enhanced crystallinity.

Figure S2. Cross-sectional SEM view of G-NiS5 without a twist angle.
Figure S3. Top-view and cross-sectional-view SEM images of (a), (c) for G-NiS10 and (b), (d) for G-NiS20. The film thickness of G-NiS10 and G-NiS20 are 3.86 µm and 6.63 µm, respectively.

Figure S4. EDX spectra measured from G-NiS5 sample.
Figure S5. (a) Band structure and (b) partial density of states (DOS) of millerite NiS.
Our calculation results coincide with the reference (S. Krishnakumar, N. Shanthi and D. Sarma, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2002, **66**, 115101-115106.), which confirms the millerite NiS is a highly covalent pd metal. The valence band and conduction band of millerite NiS mainly consist of Ni 3d and S 3p orbitals, respectively. The strong hybridization between Ni 3d and S 3p orbitals lead to metallic behavior of millerite NiS. This can be also supported by the positive numbers of DOS distributions at the Fermi level.

Figure S6. (a) SEM image of NiS NRAs grown on FTO substrate. (b) Corresponding photovoltaic performance with FTO-NiS as a CE.