Supplementary Information

1. Synthesize the redox couples. The synthesis started commercially from available isothiocyanate which were transformed into the corresponding 1-ethyl-1H-tetrazole-5-thiol (ET) derivatives by cycloaddition reaction with sodium azide in refluxing ethanol according to the known procedures. Then the oxidized specie, bis(1-ethyltetrazol-5-yl) (BET) disulfides, was prepared by oxidation of the corresponding ET with hydrogen peroxide, and thiolate (ET^-) form was obtained by deprotonation of the corresponding mercaptan (ET) with sodium bicarbonate. The structures of the above-mentioned redox couple was proved by the combination of ^{1}HNMR spectroscopy, mass spectroscopy (ESI-MS) and elemental analyses. The NMR spectra were recorded at 298 K in $CDCl_3$ at 300 MHz on a Varian Mercury-VX300 spectrometer. The chemical shifts were recorded in parts per million (ppm) with TMS as the internal reference. ESI mass spectra were determined using Finnigan LCQ Advantage mass spectrometer. Elemental analyses were performed with Thermo Quest Flash EA1112. The electrolyte consisted of 0.4 M of ET^-, 0.05 M of BET, 0.4 M 18-crown-6 (18-C-6), 0.05 M $LiClO_4$ and 0.5 M 4-tert-butylpyridine (TBP) in acetonitrile (ACN).

2. Preparation of electrodes. The NiS electrodes were electrodeposited onto a fluorine-doped tin oxide (FTO) glass substrate (13Ω/□) from an aqueous electrolyte consisting of 1M CH_4N_2S and 40mM $NiCl_2·6H_2O$ in a single-compartment glass cell with three-electrode configuration using electrochemical work station. A Pt wire and an Ag/AgCl electrode were served as auxiliary electrode and reference electrode, respectively. The periodic potential reversal (PR) techniques with different periods were undertaken in the same cathodic time and anodic time (Fig. S1). The cathodic bias and anodic bias were selected at -0.9V and 0.1V, respectively.

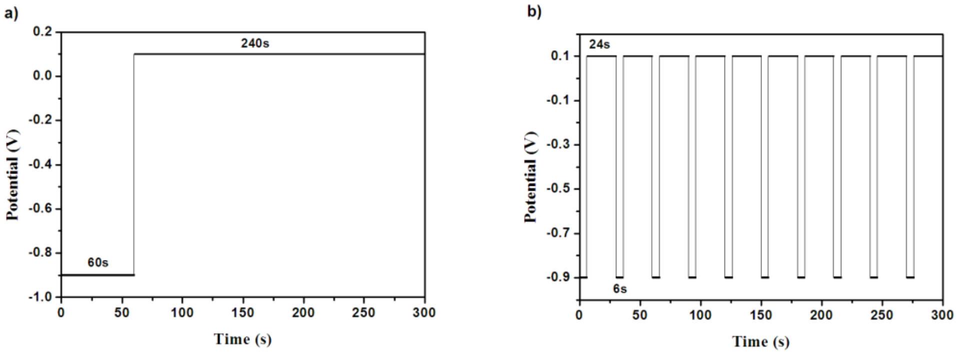

Fig. S1 The applied potential at the FTO glass *vs* time in a) PR1, b)PR10 techniques.

3. Fabricate the DSSCs. A dense TiO_2 layer was deposited on FTO glass by spray pyrolysis deposition with di-isopropoxytitanium bis(acetyl acetonate) solution and sintered at 500 °C for 30min. After that a 12μm nanoporous TiO_2 layer (PASOL HPW-18NR TiO_2 nanopowders, JGC Catalysts and Chemicals Ltd., Japan), a 4μm light reflecting spacer layer contains 25wt% 400nm TiO_2 nanopowders (JGC Catalysts and Chemicals Ltd., Japan) and 75wt% 40nm zirconia powder (Tosoh zirconia powder TZ-3Y series, Tosoh Japan). After sintered for 30 min at 500°C and cooling to 80°C, the substrate was sensitized with a 0.5 mM N719 solution for 24h. After washed with ethanol, the sensitized TiO_2 anode was encapsulated by a 100μm thick spacer of the thermo-bonding polymer (Surlyn, DuPont) with the prepared counter electrode as mentioned above through heating at 100°C. The liquid electrolyte was injected through the holes predrilled in the counter electrode, and then the hole was sealed with Surlyn polymer and cover glass.

4. Characterization. Electrochemical impedance spectroscopy (EIS) was carried out with a dummy symmetric cell composed of two electrodes separated by the electrolyte. The polymer spacer used in this case was 50 μm thick and the electrolyte was the same in the fully functional DSSCs. EIS measurements were carried out using a potentiostat (EG&G, M2273) at 0 V DC bias potential (simulated open-circuit conditions) for frequencies from 500 kHz to 100 mHz. The active surface area of the symmetrical cell was 1 cm^2. *J-V* characterization was performed using a Keithley 2400 source meter under simulated AM 1.5 sunlight illumination ($100mW\cdot cm^{-2}$) provided by an Oriel solar simulator (Model 91192, Newport Co.). A black mask with an circular aperture (0.159 cm^2) slightly smaller than the active area of the square solar cell (0.25 cm^2) was applied on top of the cell. Cyclic voltammetry for the measurement of electrochemical redox potentials was conducted on ZAHNER ENNIUM Electrochemical Workstations with a conventional three-electrode system: the working electrode was NiS electrode (0.25cm^2), the counter electrode was a Pt wire, the reference electrode was a Ag/AgCl electrode protected by a glass frit, and the supporting electrolyte was 0.1 M TBAP in anhydrous acetonitrile. The electrolyte solution was prepared by dissolving 20 mM of the reduced species, 10 mM of the oxidized species, 20 mM 18-crown-6 (18-C-6) and 0.1 M TBAP in anhydrous acetonitrile. A scanning rate of 50mV·s^{-1} was typically used for cyclic voltammetrical measurements. The potential of the reference electrode was adjusted by recording the cyclic voltammogram for 0.01 M ferrocene in anhydrous acetonitrile containing 0.1 M TBAP.

5. SEM images of the two different NiS electrodes:

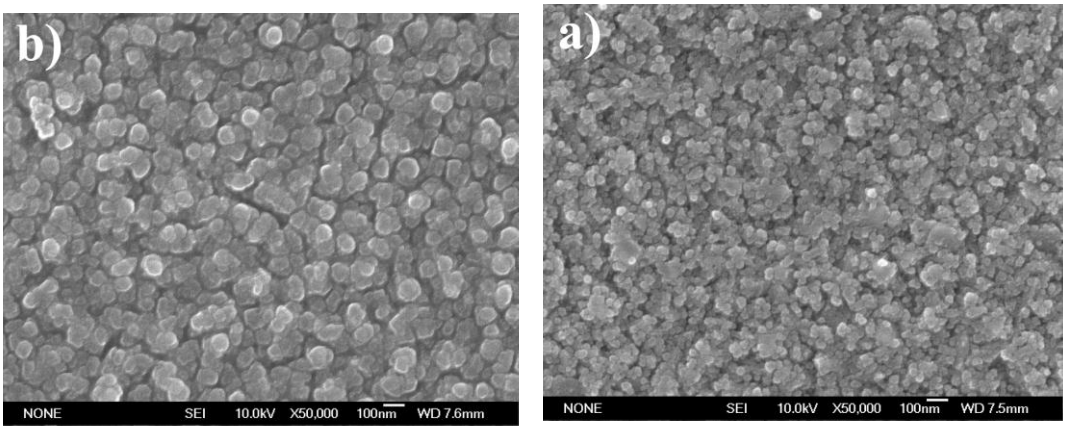

Fig. S2 The SEM images of (a) NiS_{PR10} CE and (b) NiS_{PR1} CE.