Electronic Supplementary Information

Employing Electrostatic Self-assembly of Tailored Nickel Sulfide Nanoparticles for Quasi-solid-state Dye-sensitized Solar Cells with Pt-free Counter Electrodes

Won Seok Chi, Joung Woo Han, Sungeun Yang, Dong Kyu Roh, Hyunjoo Lee*
and Jong Hak Kim*

Department of Chemical and Biomolecular Engineering, Yonsei University, 50 Yonsei-ro,
Seodaemun-gu, Seoul 120-749, South Korea

*Authors to whom correspondence should be addressed: azhyun@yonsei.ac.kr or jonghak@yonsei.ac.kr

Experimental

Synthesis of NiS nanoparticles: Rod-shaped NiS nanoparticles were synthesized by a previously reported method.[1] Ni(acacia)$_2$, 385mg, 2 ml of 1-dodecanethiol (Aldrich, 90%) and 10 ml of oleylamine (Aldrich, 90%) were put in a three-necked flask. The flask was heated to 280°C and then maintained at that temperature for 5 h with vigorous stirring and refluxing. After the flask was cooled down to room temperature, the solution was washed with hexane several times.

Synthesis of Ni_3S_2 nanoparticles: A mixture of 200 mg Ni(acacia)$_2$ (Aldrich, 95%), 50 mg cystamine (Aldrich, 95%) and 20 ml 1,5-pentanediol (Aldrich, 96%) was put in a three-necked flask. The flask was heated to 250°C and then maintained at that temperature for 30 min with vigorous stirring and refluxing. After the flask was cooled to room temperature, the solution was washed with 2-propanol several times.

Fabrication of qssDSSCs: The DSSCs with an active area of 0.16 cm^2 were constructed by drop-casting of the polymer electrolyte solution onto the photoelectrode and covering with the counter electrode, according to our previously reported procedure.[2,3] For the counter electrode, the nickel sulfide solutions dispersed in ethanol (7 mg/ml) were fully drop-casted onto the FTO glass. These films were dried in an oven at 80°C to evaporate the ethanol solvent and heat-treated to improve adhesion onto the FTO glass via electrostatic interaction between the positive charge of the nickel sulfide surface and the negative charge of the FTO surface. After the drying process, the surface of the films was wiped to eliminate excess particles. Subsequently, the prepared samples were annealed at 200°C in a N_2 atmosphere. As a reference counter electrode cell, Pt-layered FTO glass was prepared by spin-coating a 1 wt% H_2PtCl_6 solution in 2-propanol at 1500 rpm for 20 sec, followed by calcination at 450°C for 30 min. The commercial TiO_2 film pastes (18-NRT, dyesol) were screened onto the FTO glass using the doctor-blade method. These samples were dried at 50°C for 1 h, annealed at 80°C for 1 h and sintered at 450°C for 30 min to develop a 7-μm-thick nanocrystalline TiO_2 film layer. A light scattering layer was also deposited on top of the nanocrystalline TiO_2 layer using the mesoprous TiO_2 beads. The TiO_2 films were immersed in a $Ru(dcbpy)_2$ $(NCS)_2$ dye (dcbpy = 2,2-bipyridyl-4,4-dicarboxylato) solution (N719, 535-bisTBA, Solaronix, 13 mg, dissolved in 50 ml absolute ethanol) overnight for successive dye sensitization. The quasi-solid-state polymer electrolyte was composed of 0.1 g of poly(ethylene glycol) dimethyl ether (PEGDME), 0.09 g of fumed silica (particle size: 14 nm), 0.3 g of 1-methyl-3-propylimidazolium iodide (MPII), and 0.03 g of iodine (I_2) in 10 ml acetonitrile solution. After assembly, the cells were placed in a vacuum oven overnight to completely evaporate the solvent.

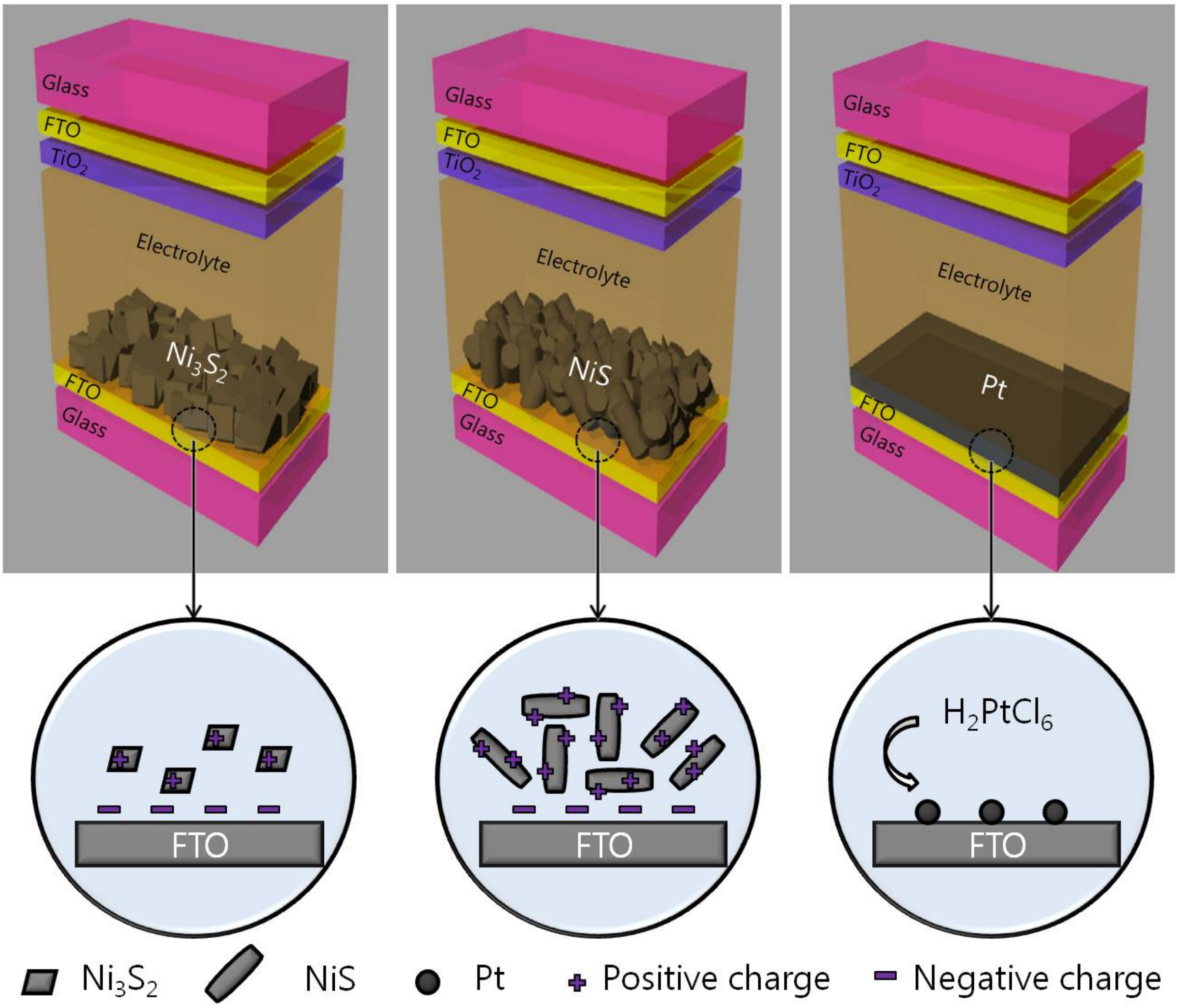
Characterization: The nickel sulfides were analyzed by TEM (JEM-2100, JEOL) equipped with EDS at an acceleration voltage of 200 kV. XRD was performed using a diffractometer (D/MAX-3500H, Rigaku Corporation Japan). XPS was analyzed by means of a K-alpha (Thermo., UK) with a monochromated Al Kα x-ray source after Ar ion sputtering by a 1 KeV beam for 1 min. CV was performed using VSP (Bio-Logic) in a conventional three-electrode electrochemical cell. Nickel sulfide-coated FTO or a Pt-coated FTO was used as the working electrode, while a platinum wire was used as the counter electrode and Ag/Ag+ (0.01 M $AgNO_3$ + 0.1M $LiClO_4$ in acetonitrile) as the reference electrode. All potentials are given versus Ag/Ag+ 0.1 M in the acetonitrile reference electrode. Zeta potential measurements were performed using a zeta potential analyzer (ZetaPlus, Brookhaven Instrument Corporation). The nickel sulfide particles and Pt deposited on the FTO glass were observed using SEM (SUPRA 55VP, Carl Zeiss Germany). The photoelectrical performance characteristics including J-V curves and EIS were measured using a solar simulator with a 100 mW/cm^2 light intensity (1000 W xenon lamp, Oriel, 91193) and an electrochemical workstation (Keithley Model 2400). The frequency range for measuring devices was 0.01 Hz to 0.1 MHz with a 0.2 V AC amplitude and the acquired curves were fitted using z-plot software.

[1] K. Aso, H. Kitaura, A. Hayashi, M. Tatsumisago, *J. Mater. Chem.* 2011, **21**, 2987-2990.

[2] S. H. Ahn, W. S. Chi, J. T. Park, J. K. Koh, D. K. Roh, J. H. Kim, *Adv Mater* **2012**, *24*, 519-522.

[3] J. K. Koh, J. Kim, B. Kim, J. H. Kim, E. Kim, *Adv Mater* **2011**, *23*, 1641-1646.

Scheme S1.


Glass
FTO
TiO_2
Electrolyte
Ni_3S_2
FTO
Glass
Glass
FTO
TiO_2
Electrolyte
NiS
FTO
Glass
Glass
FTO
TiO_2
Electrolyte
Pt
FTO
Glass
FTO
FTO
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FTO
Ni_3S_2
NiS
Pt
Positive charge
Negative charge

Fig. S1. Zeta potential of nickel sulfides in ethanol solution.

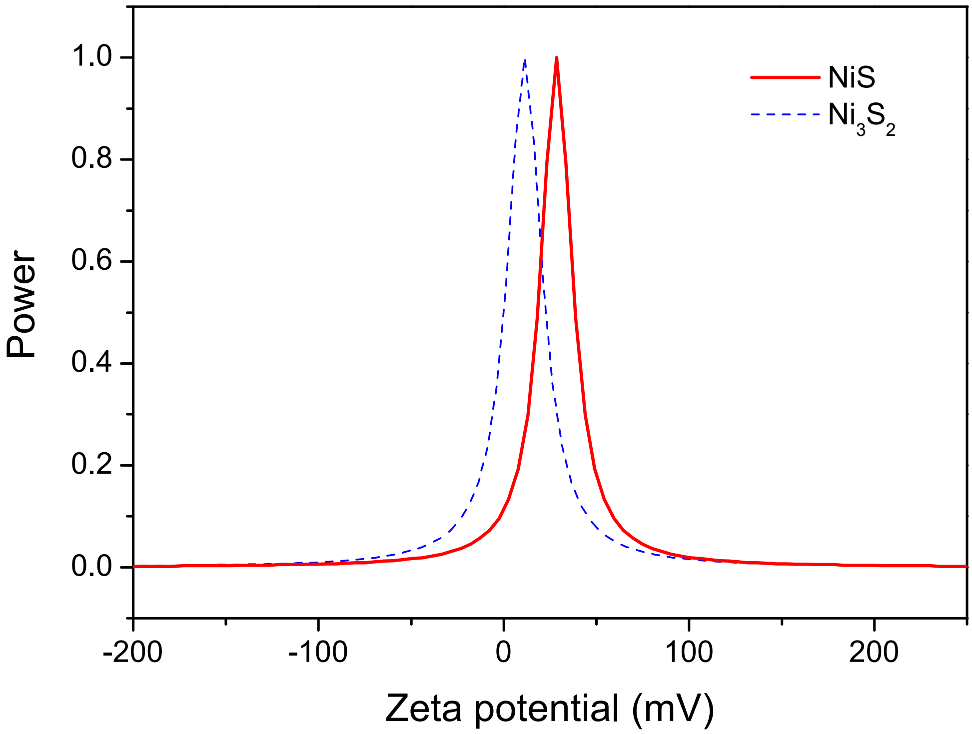


Fig. S2. XRD patterns of nickel sulfides on FTO glass.

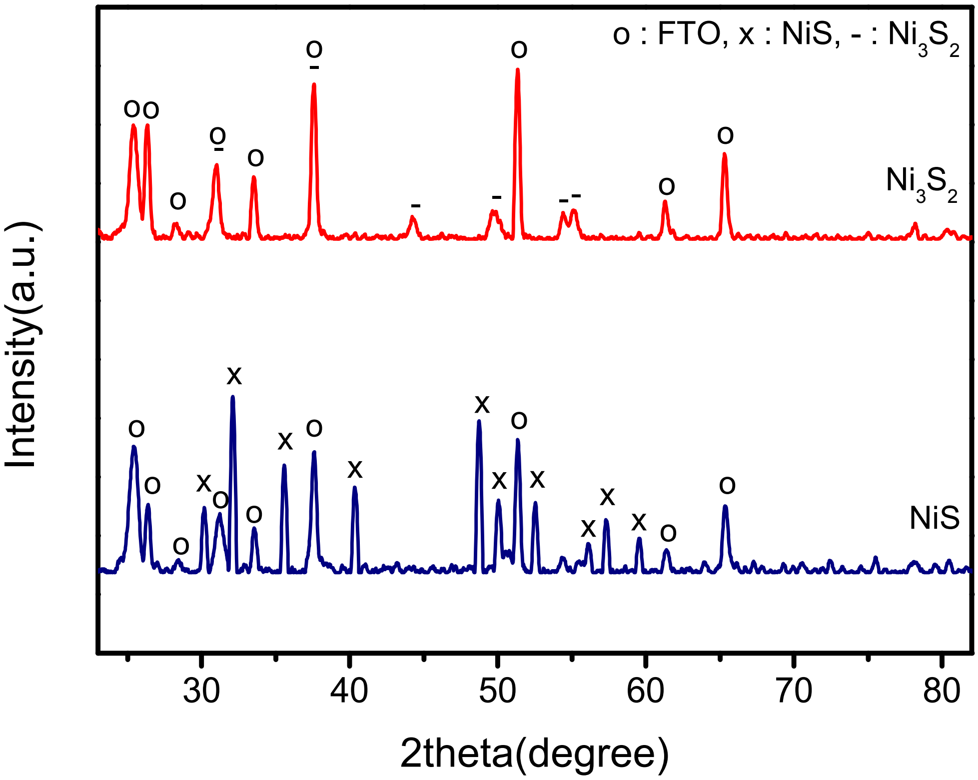


Fig. S3. XPS spectra of nickel sulfides after Ar ion etching: (a) Ni 2p, (b) S 2p.

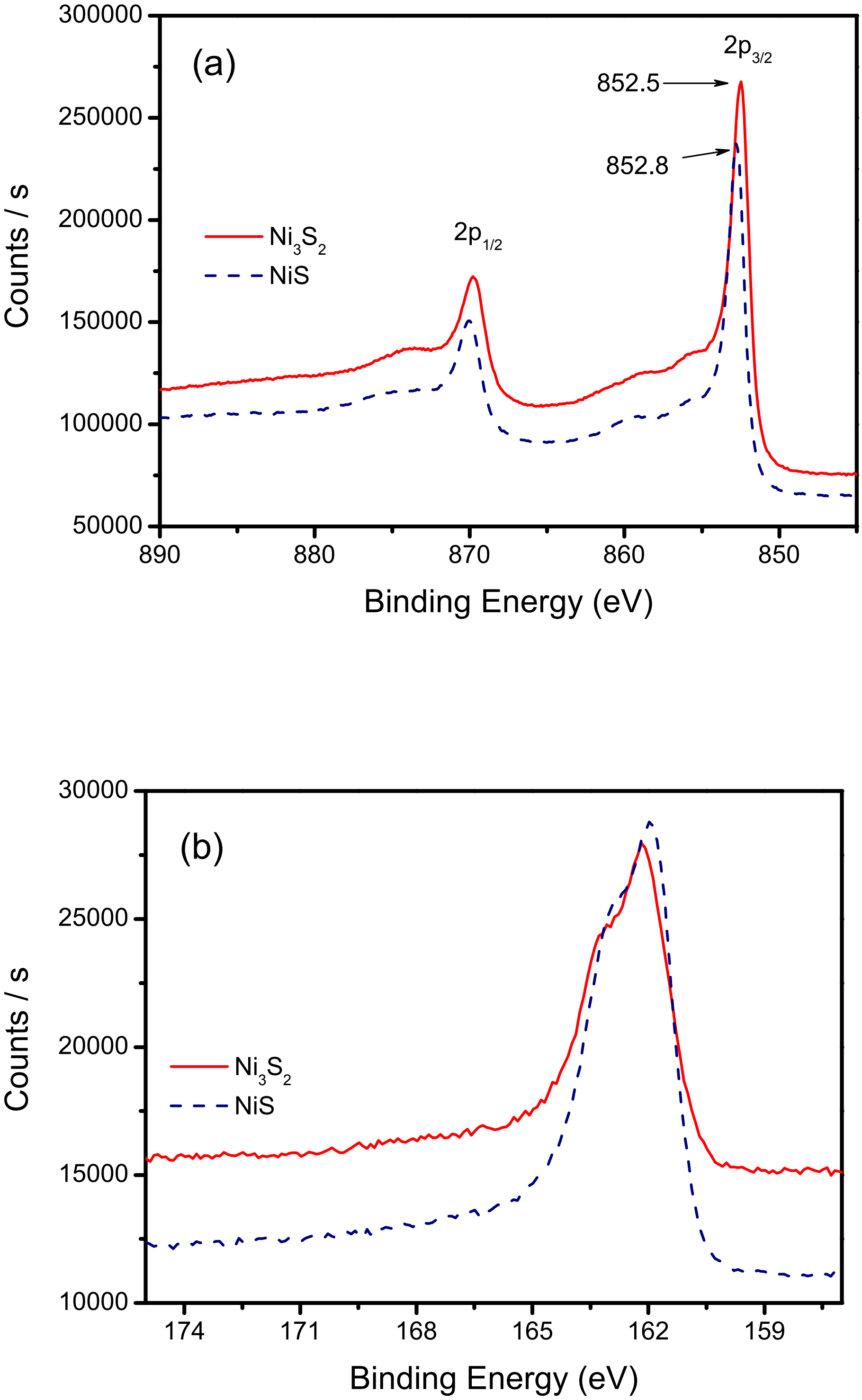


Fig. S4. Nyquist plots of the full qssDSSCs fabricated with different counter electrodes measured in dark conditions. The frequency range for devices was 0.01 Hz to 0.1 MHz.

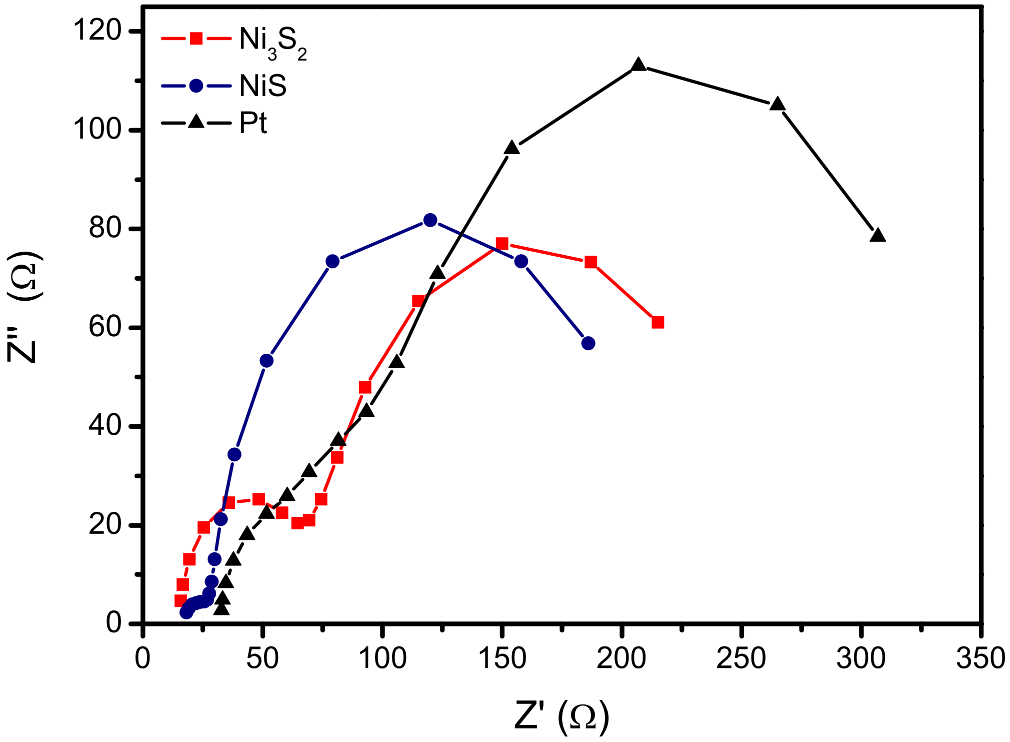


Fig. S5. Nyquist plots of the full qssDSSCs fabricated with different counter electrodes under 1 sun illumination with the frequency range from 0.01 Hz to 0.1 MHz. The inset shows the corresponding equivalent circuit.

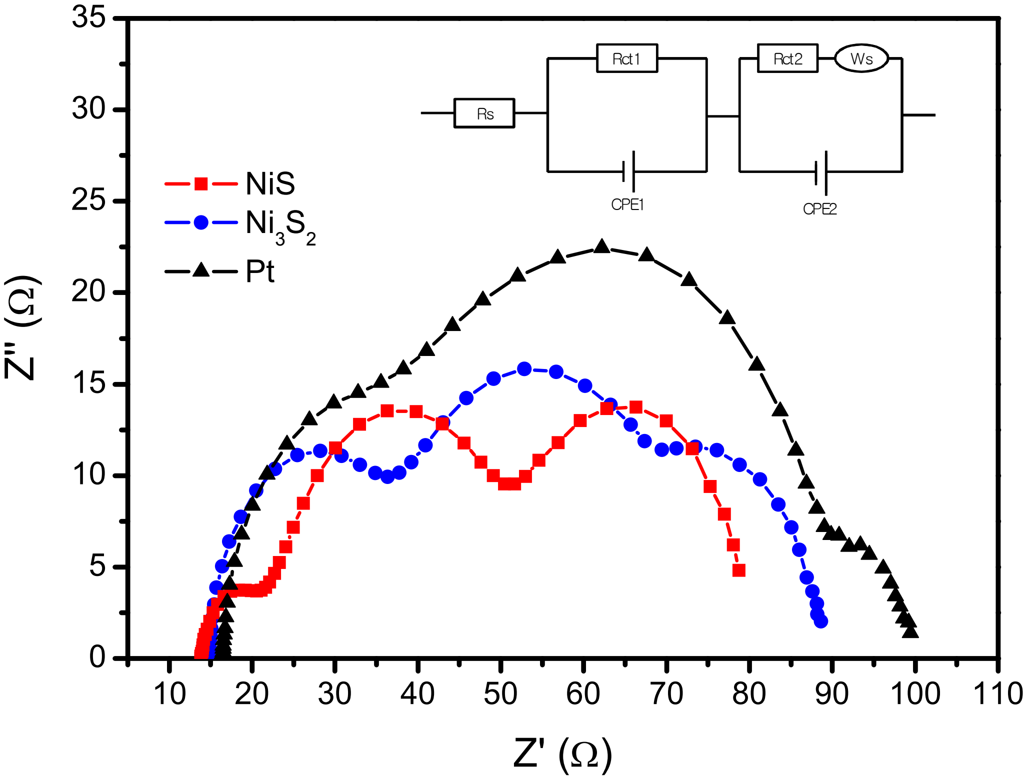
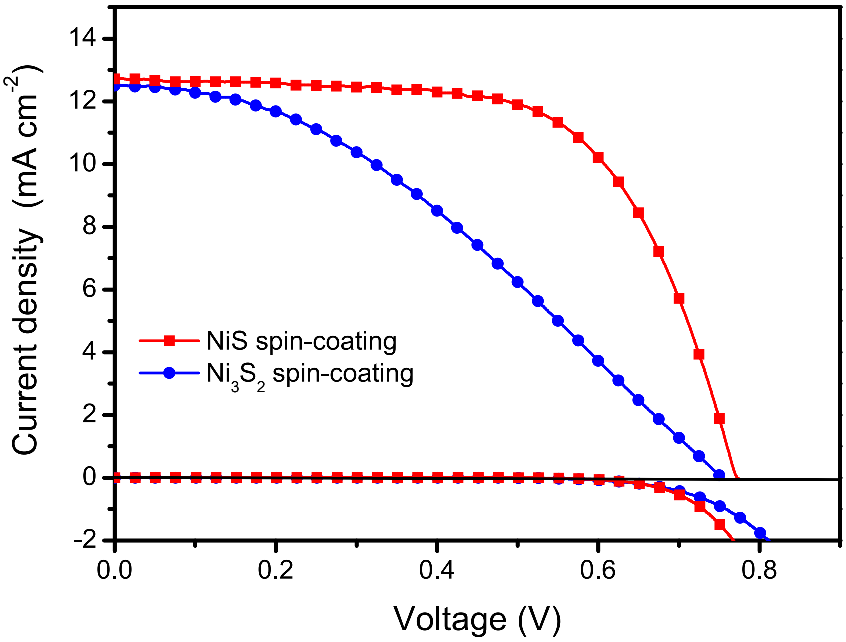


Fig. S6. (a) J-V curves and (b) Nyquist plots of qssDSSCs fabricated with two nickel sulfide counter electrodes using the spin-coating method.



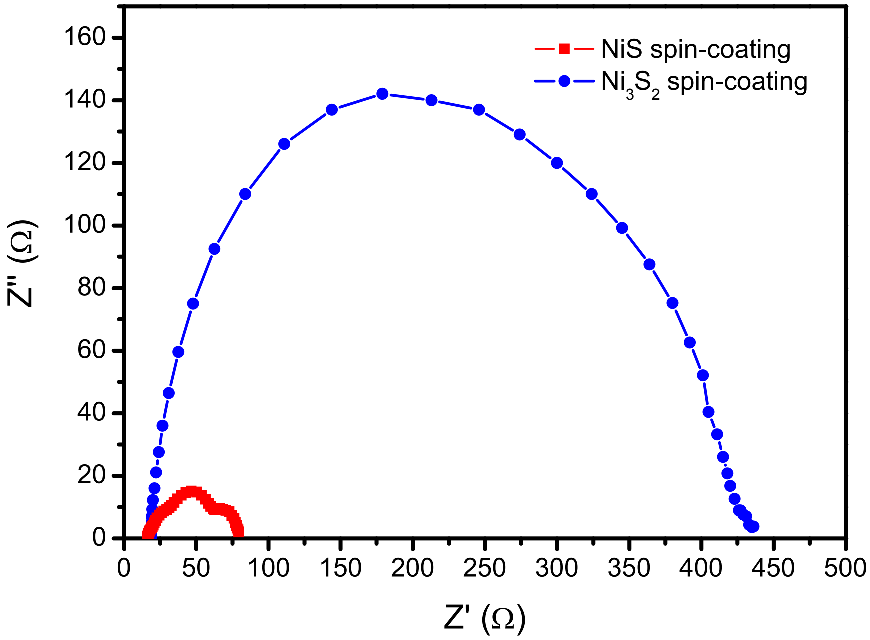


Table S1. EDX data of nickel sulfides.

	Element	Weight %	Atomic %	Uncertainty %	Correction	k-Factor
Ni_3S_2	S	22.992	35.345	0.741	0.911	1.101
	Ni	77.007	64.654	1.484	0.996	1.592
NiS	S	36.016	50.753	1.457	0.911	1.101
	Ni	63.983	49.246	2.147	0.996	1.592

Table S2. Zeta potential of nickel sulfides in ethanol solution.

	Zeta Potential (mV)	Half Width (mV)
Ni_3S_2	+ 11.3	11.2
NiS	+ 28.4	10.1

Table S3. Photovoltaic parameters of qssDSSCs fabricated with different nickel sulfide counter electrodes using the spin-coating method.

	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	Efficiency (%)	R_s (Ω)
NiS	0.76	12.7	0.63	6.2	16.2
Ni_3S_2	0.73	12.5	0.37	3.4	18.6

We found that the monolayered, deep coverage of nickel sulfides on the FTO glass via the electrostatic self-assembly using drop-casting method is most important for improving the cell performance. The qssDSSCs fabricated using a spin-coating method had lower efficiencies due to insufficient surface coverage of the nanoparticles. This resulted in larger interfacial resistances in the devices, leading to a lower fill factor. Utilization of drop-casting with higher nickel sulfide concentrations or multiple drop-casting also did not improve the cell performance, but often decreased the efficiency due to increased recombination resulting from nickel sulfide nanoparticles detached from the counter electrode.