Experimental Section

Synthesis of Binary Ni−Se Alloy CEs: The feasibility of synthesizing Ni−Se alloy CEs was confirmed by following experimental procedures: A mixing aqueous solution consisting of 2 mM H_2SeO_3 and 100 mM LiCl was made by agitating SeO_2 ultrafine powders and anhydrous LiCl in deionized water. A mixture comprising of 10 mL of above solution and 10 mL of $Ni(NO_3)_2$ aqueous solution with various concentrations was prepared as an electrolyte for Ni−Se alloy deposition [$Ni_{0.6}Se$: 1.2 mM $Ni(NO_3)_2$ + 2 mM H_2SeO_3 + 100 mM LiCl, $Ni_{0.7}Se$: 1.4 mM $Ni(NO_3)_2$ + 2 mM H_2SeO_3 + 100 mM LiCl, $Ni_{0.8}Se$: 1.6 mM $Ni(NO_3)_2$ + 2 mM H_2SeO_3 + 100 mM LiCl, $Ni_{0.9}Se$: 1.8 mM $Ni(NO_3)_2$ + 2 mM H_2SeO_3 + 100 mM LiCl, NiSe: 2.0 mM $Ni(NO_3)_2$ + 2 mM H_2SeO_3 + 100 mM LiCl, $Ni_{1.1}Se$: 2.2 mM $Ni(NO_3)_2$ + 2 mM H_2SeO_3 + 100 mM LiCl, $Ni_{1.2}Se$: 2.4 mM $Ni(NO_3)_2$ + 2 mM H_2SeO_3 + 100 mM LiCl]. The deposition of Ni−Se alloys on freshly cleaned indium tin oxide/polyethylene naphthalate (ITO/PEN, 12 Ω cm^2) was carried out on a conversional CHI660E setup comprising an Ag/AgCl reference electrode, a CE of platinum sheet, and a working electrode of ITO/PEN substrate. A cyclic voltammetry mode was applied in a potential range of −0.9 ~ 1.4 V. The scan rate and scanning number were controlled at 10 mV s^{-1} and 1 cycle, respectively.

Synthesis of Ti Foil Reserved TiO_2 Anodes: The Ti foil (99.9% in purity and 80 μm in thickness) with a size of 1.5 cm × 1.5 cm was carefully rinsed by acetone/water, ethanol/water, acetone, ethanol, water, and ethanol. An active area of around 0.5 cm × 0.5 cm was etched by 10 wt% HF aqueous solution. After being thoroughly rinsed by deionized water, the groove was filled by prepared TiO_2 colloid.[S1,S2] Ti foil reserved TiO_2 anode was obtained by calcined in a muffle furnace at 450 ºC for 30 min. Finally, the TiO_2 film was sensitized by 0.25 mmol dm^{-3} N719 ethanol solution for 24 h.

Assembly of DSSCs: The flexible DSSC was fabricated by sandwiching redox electrolyte between a dye−sensitized TiO_2 anode and a Ni−Se CE. A Surlyn film (30 μm in thickness) was utilized to seal the flexible DSSC through hot−pressing. A redox electrolyte consisted of 100 mM of tetraethylammonium iodide, 100 mM of tetramethylammonium iodide, 100 mM of tetrabutylammonium iodide, 100 mM of NaI, 100 mM of KI, 100 mM of LiI, 50 mM of I_2, and 500 mM of 4−tert−butyl−pyridine in 50 ml acetonitrile.

Electrochemical Characterizations: The electrochemical performances were recorded on a conventional CHI660E setup comprising an Ag/AgCl reference electrode, a CE of Pt sheet, and a working electrode of FTO glass supported Ni−Se alloy. The CV curves were recorded in a supporting electrolyte consisting of 50 mM M LiI, 10 mM I_2, and 500 mM $LiClO_4$ in acetonitrile. EIS measurements were also carried out in a frequency range of 0.1 Hz ~ 10^5 kHz and an ac amplitude of 10 mV at room temperature. Tafel polarization curves were recorded by assembling symmetric dummy cell consisting of CE|redox electrolyte|CE.

Photovoltaic Measurements: The photovoltaic test of the DSSC with an active area of 0.25 cm^2 was carried out by measuring the photocurrent−voltage (*J*−*V*) characteristic curves using a CHI660E Electrochemical Workstation under irradiation of a simulated solar light from a 100 W Xenon arc lamp (XQ−500 W) in ambient atmosphere. The incident light intensity was controlled at 100 mW cm^{-2} (calibrated by a standard silicon solar cell). A black mask with an aperture area of around 0.25 cm^2 was applied on the surface of DSSCs to avoid stray light completely.

Supplentary references

S1 S. S. Yuan, Q. W. Tang, B. L. He, L. Men, H. Y. Chen, *Electrochim. Acta*, 2014, **125**, 646.

S2 B. B. Hu, Q. W. Tang, B. L. He, L. Lin and H. Y. Chen, *J. Power Sources*, 2014, **267**, 445.

Supplentary Tables

Table S1. Photovoltaic parameters of DSSCs with varied CEs and the simulated data from EIS spectra.[a]

CEs	η (%)	V_{oc} (V)	J_{sc} (mA cm^{-2})	*FF* (%)	R_{ct} (Ω cm^2)
$Ni_{0.6}Se$	2.33	0.67	4.98	69.8	2.74
$Ni_{0.7}Se$	2.61	0.71	5.41	67.9	2.10
$Ni_{0.8}Se$	3.25	0.68	8.60	55.6	1.07
$Ni_{0.9}Se$	5.27	0.73	9.72	74.3	0.37
NiSe	7.35	0.69	17.52	60.8	0.21
$Ni_{1.1}Se$	5.54	0.71	12.42	54.1	0.35
$Ni_{1.2}Se$	3.04	0.69	5.77	76.4	1.52

[a] V_{oc}: open−circuit voltage; J_{sc}: short−circuit current density, *FF*: fill factor; η: power conversion efficiency; R_{ct}: charge−transfer resistance.

Table S2. Photovoltaic parameters of DSSCs with NiSe CE and anodes at varied groove depths.

Groove depth (μm)	η (%)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)
0	3.18	0.71	7.16	62.6
30	4.60	0.68	9.99	67.7
33	4.97	0.72	10.26	67.3
36	7.35	0.69	17.52	60.8
39	6.02	0.71	12.93	65.6
42	4.54	0.73	8.37	74.3
48	4.40	0.70	9.94	63.2
57	4.14	0.74	7.74	72.3
66	3.48	0.69	7.25	69.6

Supplentary Figures

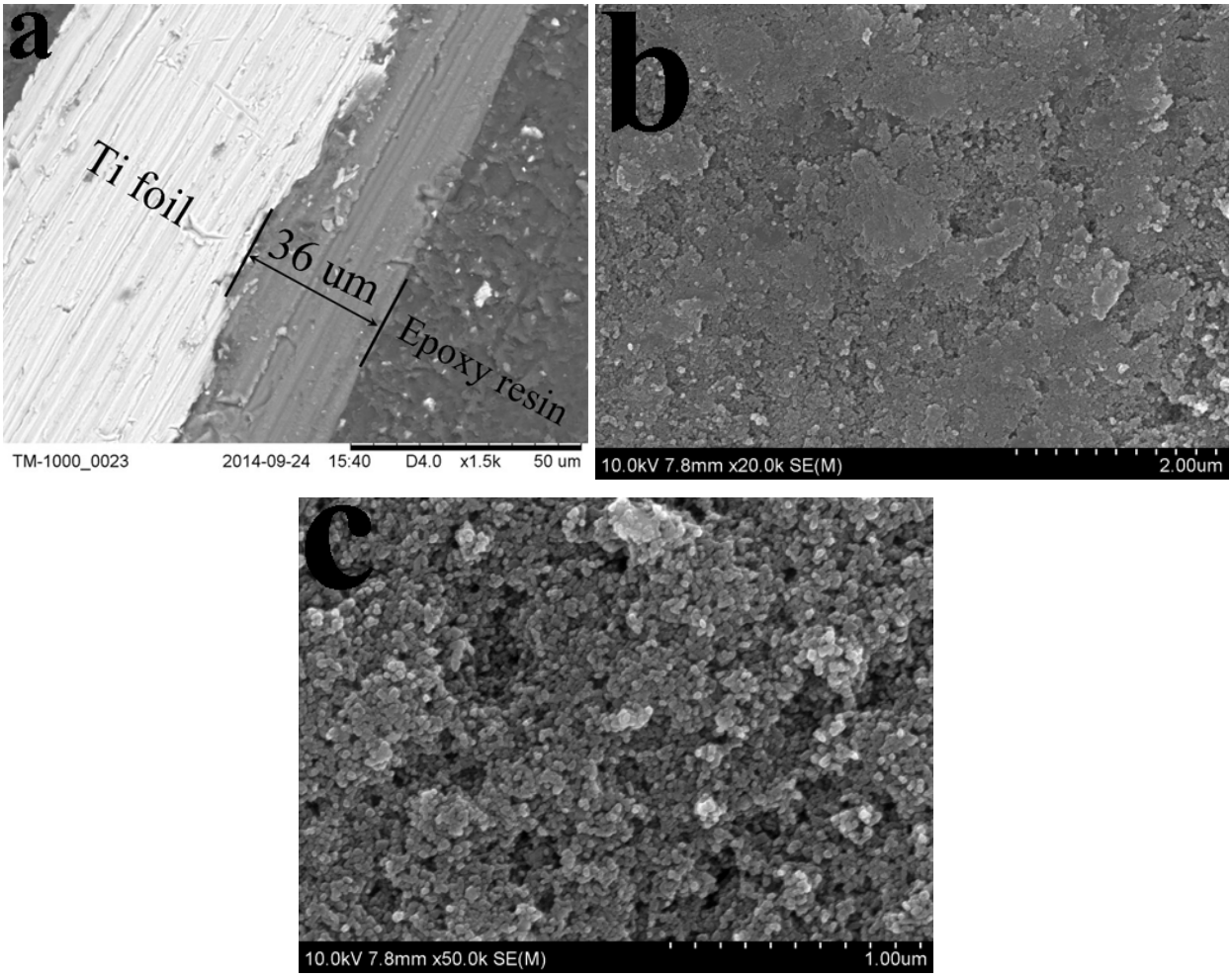

Fig. S1. (a) Cross−sectional SEM image of Ti foil supported TiO_2 film with a thickness of around 36 μm. (b) & (c) Top−view SEM images of TiO_2 film. The average particle size of TiO_2 is around 200 nm.

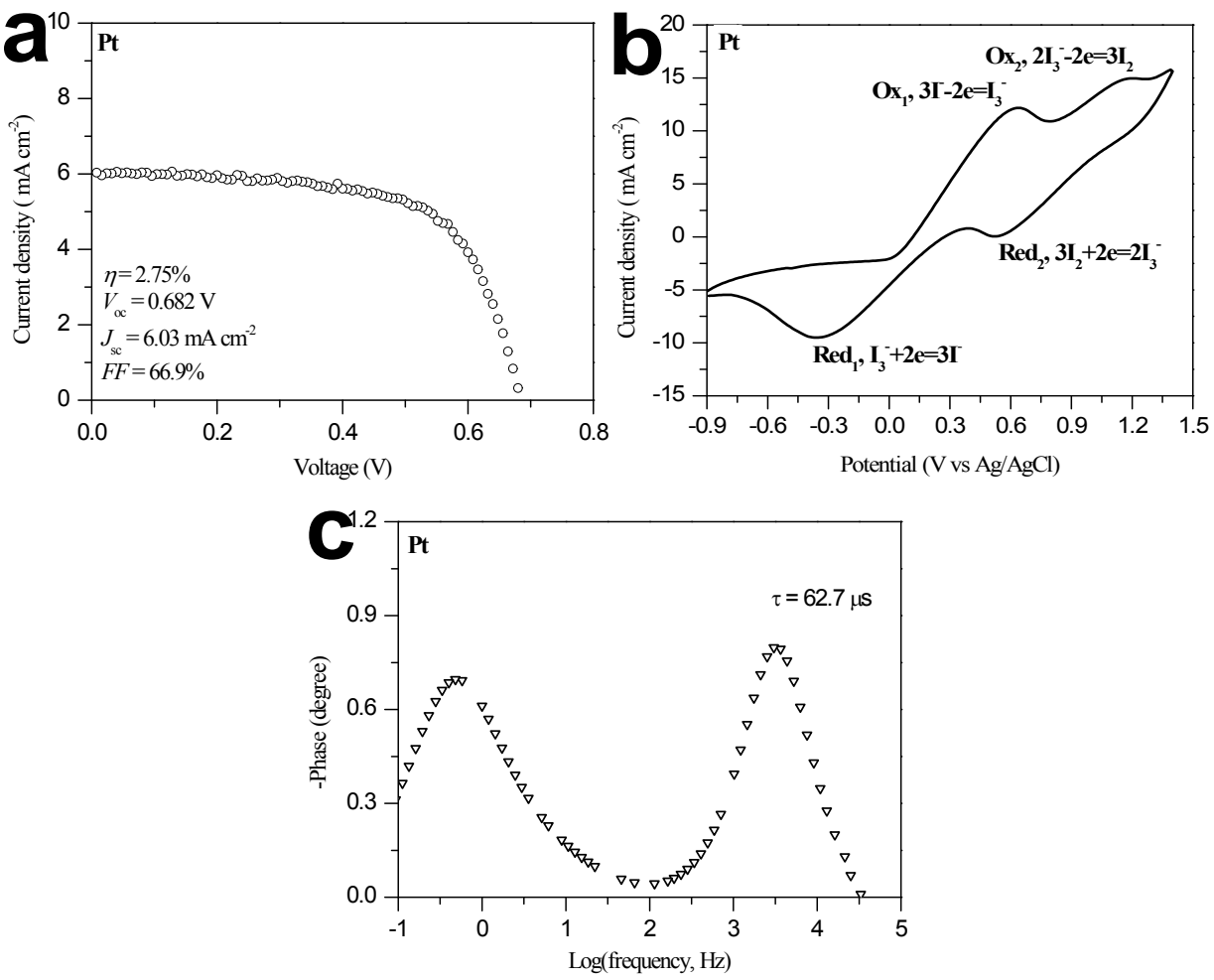

Fig. S2. (a) *J*−*V* curve of the DSSC with flexible Pt electrode. (b) CV curves of flexible Pt CE at a scan rate of 50 mV s^{-1}. (c) Bode EIS plot of the symmetric dummy cell from two identical Pt electrodes.

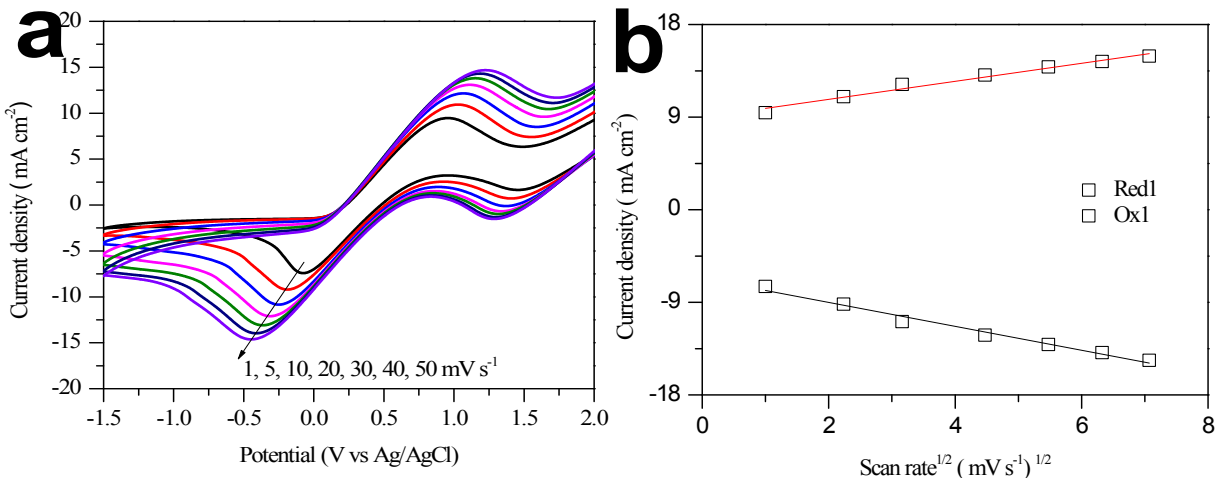

Fig. S3. (a) CV curves of NiSe alloy CE at various scan rates. (b) Linear relationships between square root of scan rate and peak current densities.

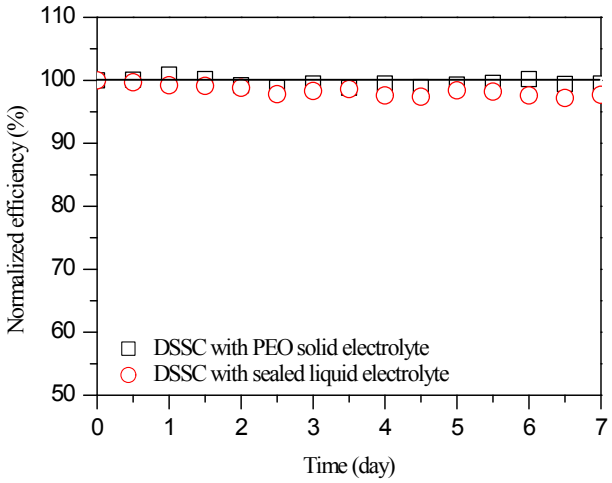

Fig. S4. Normalized efficiencies of the DSSCs with I^-/I_3^- doped poly(ethylene oxide) solid electrolyte and groove sealed liquid electrolyte in the current work. The feasibility of synthesizing I^-/I_3^- doped PEO solid−state electrolyte was confirmed by following experimental procedures: A mixing solution consisting of I^-/I_3^- redox couples and PEO (M_w = 2,000,000) was made by agitating 0.1 g of LiI, 0.019 g of I_2, and 0.264 g of PEO. After vigorous agitating for 24 h, the viscous reactant was casted onto dye−sensitized TiO_2 anode for consolidation at vacuum.