

Experimental Details

Preparation of Ti Wire Supported TiO₂ Nanotube Anodes: The Ti wires ($\Phi = 0.2$ mm) were thoroughly rinsed with acetone, ethanol, and deionized water, subsequently polished for 10 min with mixture from HF (1 wt%), HNO₃ (7 wt%), and deionized water. The volume ratio was controlled at 1: 4: 5 for HF: HNO₃: H₂O. The Ti wire supported TiO₂ nanotubes were prepared by an anodic oxidation method using Ti wire as a working electrode, Pt sheet as a counter electrode, and mixture of 0.3 wt% NH₄F/ethanol/H₂O as a supporting electrolyte. The reaction was performed at 60 V for 5 h. Subsequently, the Ti wire supported TiO₂ nanotubes were annealed at 450 °C for 3 h. The resultant anodes were further sensitized by immersing into a 0.50 mM ethanol solution of N719 dye.

Preparation of MSe CEs: Required amount of indium nitrate was dissolved in diacetylmethane using DEA as an additive. After being refluxed at 60 °C for 3 h, the stannic chloride (The molar ratio of In to Sn was 10: 1) was dissolved in ethanol to form a homogeneous solution, which was added in the abovementioned indium nitrate solution to obtain ITO sol. The freshly cleaned quartz tube ($\Phi = 5$ mm, $d = 1$ mm) was immersed into ITO sol, dried with air, and calcined at 550 °C for 30 min. By repeating the steps for 10 times, quartz tube supported ITO substrate was obtained.

The feasibility of synthesizing MSe alloy CEs was confirmed by the experimental procedures: A mixing aqueous solution consisting of H₂SeO₃ and LiCl was made by agitating 0.0222 g of SeO₂ ultrafine powers and 0.6041 g of LiCl. 2 mM of stoichiometric CoCl₂ (NiCl₂ or FeCl₂) was dissolved in the above solution, and the total volume was adjusted to 100 mL by deionized water. The CoSe, NiSe, or FeSe CE was synthesized by a cyclic voltammetry method using quartz tube supported ITO substrate as a working electrode, Ag/AgCl as a reference electrode, and Pt sheet as a counter electrode. The scan rate was 50 mV s⁻¹ and the reaction temperature was room temperature.

As a reference, the Pt CE was also performed in 2 mM H_2PtCl_6 aqueous solution on quartz tube supported ITO substrate.

DSSC Assembly: The cylindrical DSSC was fabricated by inserting dye-sensitized TiO_2 nanotubes (on Ti) into quartz tube supported CEs, filled with I^-/I_3^- redox electrolyte and plugged with ethylene vinyl acetate copolymer. 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. The ethylene vinyl acetate copolymer was heated to its molten state and then injected into the two ends of tubes for consolidation.

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 cylindrical CE. The cyclic voltammetry (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 of the DSSCs were also carried out in a frequency range of 0.1 Hz \sim 10^5 kHz and an ac amplitude of 10 mV at room temperature.

Photovoltaic Measurements: The photovoltaic test of the DSSC 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). The cylindrical DSSC was rotated to measure the J - V curves at different incident angles. The active area for calculating J_{sc} and η was the geometric project area of photoanode, therefore it was the diameter ($\Phi = 0.2 \text{ mm}$) of Ti wire. A mask was placed on the top of DSSC to avoid stray light. The fill factor (FF) and light-to-electric energy conversion efficiency

(η) was calculated according to the equations:

$$FF = \frac{P_{\max}}{J_{sc} \times V_{oc}} = \frac{J_{\max} \times V_{\max}}{J_{sc} \times V_{oc}}$$
$$\eta(\%) = \frac{P_{\max}}{P_{in}} \times 100\% = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}} \times 100\%$$

where J_{sc} is the short-circuit current density ($\text{mA}\cdot\text{cm}^{-2}$), V_{oc} is the open-circuit voltage (V), P_{in} is the incident light power, P_{\max} is the maximum power output, J_{\max} ($\text{mA}\cdot\text{cm}^{-2}$) and V_{\max} (V) are the current density and voltage at the point of maximum power output in the J - V curves, respectively.

Other Characterizations: The optical transmission spectra of resultant CEs were recorded on a UV–vis spectrophotometer at room temperature. X-ray diffraction (XRD) profile of the resultant TiO_2 nanotubes was recorded on an X-ray powder diffractometer (X'pert MPD Pro, Philips, Netherlands) with Cu $K\alpha$ radiation ($\lambda = 1.542\text{\AA}$) in the 2θ range from 20 to 70° operating at 40 kV accelerating voltage and 40 mA current). The morphologies of the resultant MSe CEs were observed with a transmission electron microscopy (TEM, JEM2010, JEOL). The work functions were achieved by a SKP RCH020 Kelvin probe, which features a stainless gold tip as a reference electrode. The contact potential difference was defined as the work function of the tip minus the work function of sample. The IPCE was measured as a function of wavelength from 400 to 700 nm by using a monochromator (Forster Tech).

Table S1. The photovoltaic and electrochemical parameters for the cylindrical DSSCs.

CEs	η (%)	V_{oc} (V)	FF (%)	J_{sc} (mA cm ⁻²)	R_{ct1} (Ω cm ²)	R_{ct2} (Ω cm ²)
FeSe	3.18	0.696	58.1	7.86	4.85	17.08
CoSe	6.42	0.716	70.8	12.66	2.08	6.12
NiSe	5.07	0.700	76.2	9.50	8.13	27.56
Pt	2.84	0.654	57.5	7.55	9.34	32.96

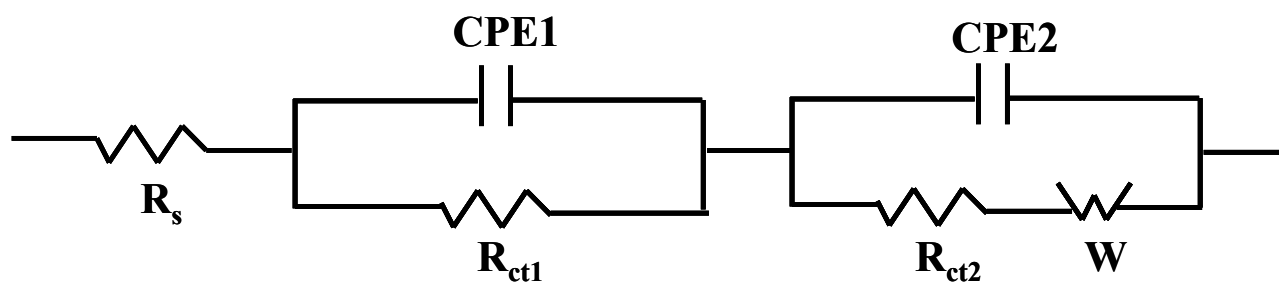


Fig. S1 The equivalent circuit for the EIS plots of cylindrical DSSCs. R_s : sheet resistance; R_{ct1} : charge-transfer resistance at counter electrode/electrolyte interface; R_{ct2} : charge-transfer resistance at TiO_2 /dye/electrolyte interface; W : Nernst diffusion impedance corresponding to the diffusion resistance of I^-/I_3^- redox couples; CPE1 and CPE2 are constant phase elements.

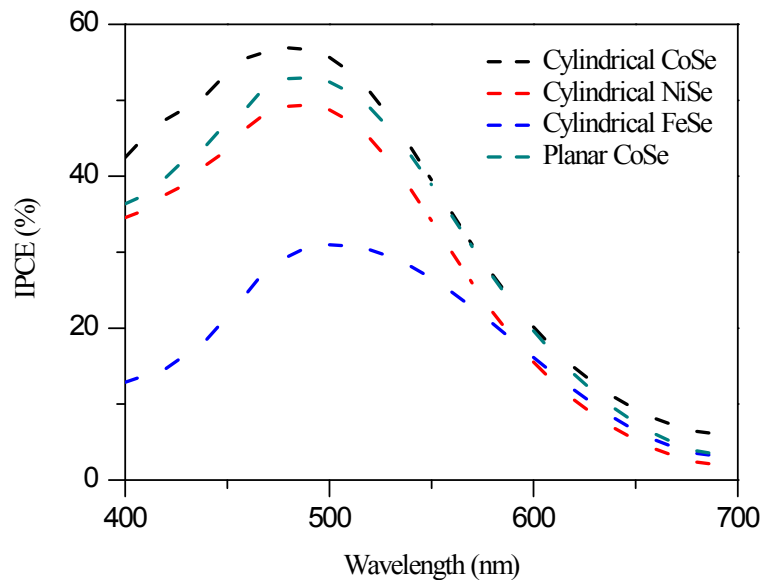


Fig. S2 The IPCE spectra of the cylindrical DSSCs with CoSe, NiSe, or FeSe CEs and planar DSSC device with CoSe CE.

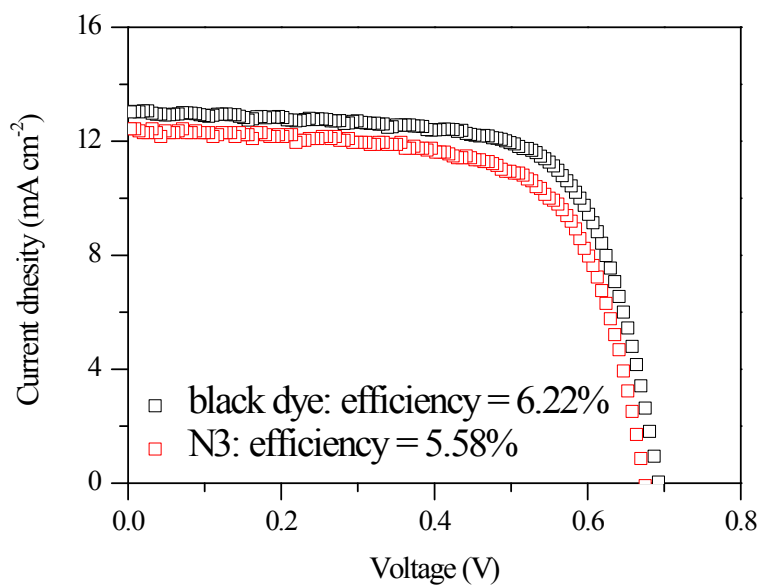


Fig. S3 The J-V curves for the DSSCs with CoSe CE and black dye or N3 dye.

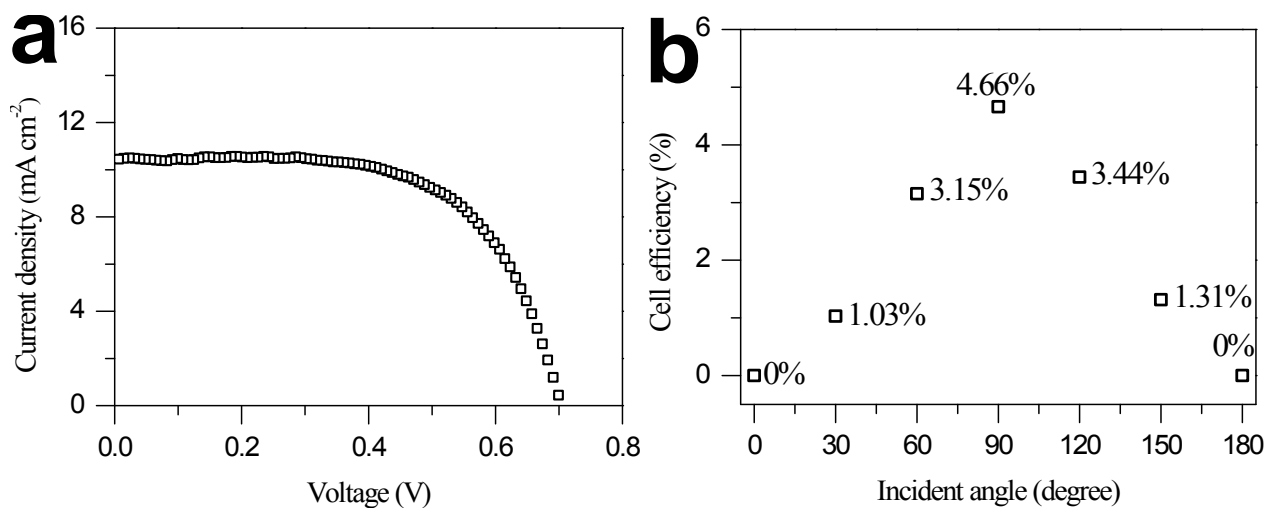


Fig. S4 (a) The J-V curve for the planar DSSC with N719 sensitized TiO₂ nanotube anode on Ti foil, CoSe CE, and I⁻/I₃⁻ redox electrolyte. (b) Cell efficiencies as a function of incident angle.