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 They were 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 further sensitized by immersing into a 0.5 mM ethanol solution of N719.

Preparation of counter electrodes: The feasibility of synthesizing CoSe counter electrode was confirmed by the following experimental procedures. In details, a mixing aqueous solution consisting of H_2SeO_3 and LiCl was made by agitating 0.0222 g of SeO₂ ultrafine powers and 0.6041 g of LiCl. 2 mM of stoichiometric CoCl₂ was dissolved in the above solution, and the total volume was adjusted to 100 mL by deionized water. In the case of Pt₃Ni electrode, the freshly-cleaned Ti wire was immersed into an aqueous solution containing 3 mM H_2PtCl_6 , 1 mM NiSO₄ to produce Pt₃Ni electrode. The CoSe and Pt₃Ni counter electrodes were synthesized by a cyclic voltammetry method using Ti wire as a working electrode, Ag/AgCl as a reference electrode, and Pt sheet as a counter electrode. The deposition window ranged from -0.4 to 1.2 V at a scan rate of 50 mV s⁻¹ for four cycles. The reaction

temperature was controlled at room temperature. As a reference, the Pt electrode was also performed in 2 mM H_2PtCl_6 aqueous solution on Ti wire.

DSSC assembly: The optical fiber induced DSSC was fabricated by inserting a dyesensitized TiO₂ nanotubes (on Ti) and a counter electrode (CoSe, Pt₃Ni or Pt) into a hollow optical fiber filled with an I^{-}/I_{3}^{-} oxidation-reduction electrolyte. Subsequently, the LPP phosphors were coated on the external surface of hollow optical fiber. The ends were sealed with an ethylene-vinyl acetate copolymer. Finally, the whole device was inserted into a transparent quartz tube. The 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 I₂ 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 one 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 Ti wire CE. The cyclic voltammetry (CV) curves were recorded in a supporting electrolyte consisting of 50 mM LiI, 10 mM I₂ and 500 mM LiClO₄ in acetonitrile. EIS measurements of the DSSCs were also carried out in a frequency range of 0.1 Hz~10⁵ kHz and an ac amplitude of 10 mV at room temperature.

Photovoltaic measurements: The photovoltaic test of the optical fiber induced DSSC was carried out by measuring the photocurrent-voltage (J-V) characteristic curves

using a CHI660E Electrochemical Workstation by illuminating hollow optical fiber by 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 active area for calculating J_{sc} and η was the geometric project area of photoanode, therefore it was the diameter ($\phi = 0.2$ mm) of Ti wire. The fill factor (*FF*) and power conversion efficiency (η) was calculated according to the equations:

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

where J_{sc} is the short-circuit current density (mA cm⁻²), V_{oc} is the open-circuit voltage (V), P_{in} is the incident light power, P_{max} in the maximum power output, J_{max} (mA 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: 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 α radiation ($\lambda = 1.542$ Å) in the 2θ range from 20-70 °C operating at 40 kV accelerating voltage and 40 mA current.

Supporting tables and figures

Table S1 The electrochemical parameters of various CEs obtained from EIS

characterization.

CEs	$R_{\rm s} \left(\Omega \ { m cm}^2 ight)$	$R_{\rm ct} (\Omega { m cm}^2)$	$W(\Omega \text{ cm}^2)$
CoSe	3.923	6.235	3.302
Pt ₃ Ni	4.293	7.387	3.546
Pt	4.185	13.050	4.750



Fig. S1 The cross-sectional SEM image of as-prepared TiO_2 nanotube arrays.



Fig. S2 CV curves of Pt_3Ni counter electrode in I^-/I_3^- redox electrolyte recorded at varied scan rates.



Fig. S3 Relationship between peak current densities and square root of scan rates.



Fig. S4 Nyquist EIS plots of various solar cells based on CoSe, Pt₃Ni and Pt counter electrodes, respectively. The equivalent circuit for the EIS plots of optical fiber DSSCs. R_s : sheet resistance; R_{ct1} : charge-transfer resistance at counter electrode/electrolyte interface; R_{ct2} : charge-transfer resistance at TiO₂/dye/electrolyte interface; W: Nernst diffusion impedance corresponding to the diffusion resistance of I-/I₃⁻ redox couples; CPE1 and CPE2 are constant phase elements.



Fig. S5 The on-off switches of optical fiber induced DSSCs by alternatively irradiating (100 mW cm⁻²) and darkening (0 mW cm⁻²) the devices.



Fig. S6 The PL spectrum of LPP phosphors and the absorbance spectrum of N719 dye.



Fig. S7 Characteristic *J-V* curves of DSSCs with and without LPP phosphors using (a) Pt_3Ni and (b) CoSe counter electrodes.



Fig. S8 Dark *J-V* characteristics of various solar cells.