Supporting Information

Hierarchical $TiO_{1.1}Se_{0.9}$-wrapped carbon cloth as the TCO-free and Pt-free counter electrode for iodide-based and cobalt-based dye-sensitized solar cells

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Materials

Conductive substrates: Fluorine–doped tin oxide glass (FTO, TEC–7, 7 Ω $sq.^{-1}$) was purchased from NSG America, Inc., New Jersey, USA; carbon cloth (CC, W0S1002, thickness = 0.36 mm, basic weight = 120 g cm^{-2}, sheet resistance = 0.60 Ω $sq.^{-1}$) was bought from CeTech Co., Ltd., Taiwan. Precursors: The titanium precursor, titanium(IV) tetraisoproproxide (TTIP, >98%), was obtained from Sigma Aldrich, while the selenide precursor, selenium (Se) pellet, was furnished by Nilaco Corporation, Tokyo, Japan. Solvents: Ethanol (EtOH, 99.5%), 2–methoxyethanol (99.8%), and isopropyl alcohol (IPA, 99.5%) were supplied by Sigma Aldrich. Acetonitrile (ACN, 99.99%) and nitric acid (HNO_3, *ca.* 65% solution in water) was procured from J. T. Baker. Acetone (99%), 4–tert–butylpyridine (tBP, 96%), and tert–butyl alcohol (tBA, 96%) were the commercial products from Acros. 3–Methoxypropionitrile (MPN, 99%) was received from Alfa Aesar. Electrolyte: Lithium iodide (LiI, synthetical grade), iodine (I_2, synthetical grade), and lithium perchlorate ($LiClO_4$, ≥98.0%) were distributed by Sigma Aldrich. 1,2-Dimethyl-3-propylimidazolium iodide (DMPII) was provided by Tokyo Chemical Industry Co., Ltd. Commercial TiO_2: Transparent TiO_2 paste (TL paste, Ti–nanoxide HT/SP, 13 nm) was delivered by Solaronix (S.A., Aubonne, Switzerland). Light scattering TiO_2 particles (ST–41, with an average diameter of 200 nm) were got from Ishihara Sangyo, Ltd. Another commercial light scattering TiO_2 particle (US3547, rutile, average size = 300 nm) was obtained from US Research Nanomaterials Inc., Houston, USA. *Polymers:* Poly(ethylene glycol) (PEG, MW~20,000) was acquired from Merck. Surlyn® (SX1170–60, 60 μm) was the product from Solaronix. *Dye:* Cis-diisothiocyanato bis(2,2'–bipyridyl–4,4'–dicarboxylato) ruthenium (II) bis(tetrabutylammonium) (N719 dye) was obtained from Luminescence Technology Corp., Taiwan. An organic dye for cobalt-based electrolyte system, HL5, was supplied by Prof. Jiann T. Lin's group in Institute of Chemistry, Academia Sinica.

Synthetic procedure of cobalt redox mediators

Unless otherwise specified, all the reactions were performed under N_2 atmosphere, using standard Schlenk techniques. All the chemicals used in this work were of the purist quality available. The reduced-state cobalt mediator, tris(1,10-phenanthroline)cobalt di(bis(trifluoromethane)sulfonimide) ($Co^{II}(Phen)_3(TFSI)_2$), was prepared via a three-step procedure as follow. (1) Cobalt(II) chloride hexahydrate ($CoCl_2 \cdot 6H_2O$, 2.38 g, 10 mmol) was dissolved in 15 ml EtOH, and 1,10-phenanthroline (5.9469 g, 33 mmol) was dissolved in 10 ml EtOH. (2) The precursor of 1,10-phenanthroline were dropwise added into the precursor of $CoCl_2 \cdot 6H_2O$ solution, and then the mixed solution was kept at 70 ^oC for at least 2 h. (3) A solution containing bis(trifluoromethane)sulfonimide lithium salt (LiTFSI, 6.32 g, 22 mmol) in EtOH was added into the previous solution to obtain the light yellow precipitate of $Co^{II}(Phen)_3(TFSI)_2$. The product was collected by filtration, washed by organic solvents (EtOH, de-ionic water, diethyl ether, acetonitrile *etc.*) several times, and dried in vacuum. The oxidized-state cobalt mediator, tris(1,10-phenanthroline)cobalt tri(bis(trifluoromethane)sulfonimide) ($Co^{III}(Phen)_3(TFSI)_3$), was prepared similarly as follow. (1) $CoCl_2 \cdot 6H_2O$ (0.50 g, 2.1 mmol) was dissolved in 5 ml de-ionic water, and 1,10-phenanthroline (1.26 g, 7 mmol) was dissolved in 5 ml MeOH; the latter solution was dropwise added into the former solution, and then the mixed solution was kept at 70 ^oC for at least 2 h. (2) A methanolic bromine solution (0.29 g, 1.8 mmol in 5 ml) was added in previous mixture to obtain the chrome yellow precipitate immediately. This chrome yellow precipitate is collected by filtration, washed by organic solvents (EtOH, de-ionic water, diethyl ether, acetonitrile *etc.*) several times, and dried in vacuum. (3) Then the chrome yellow precipitate was dissolved in de-ionic water, and then mixed with an aqueous solutions of LiTFSI (2.01 g, 7 mmol); accordingly, the products of $Co^{III}(Phen)_3(TFSI)_3$ was collected by filtration, washed by organic solvents (EtOH, and diethyl ether) several times, and dried in vacuum.

Analytic techniques

Physical properties: X–ray diffraction (XRD) spectroscopy (Rigaku, Tokyo, Japan) and X–ray photoelectron spectroscopy (XPS, Thermo Scientific Theta Probe, UK) were used to investigate crystalline phases and elemental bindings of the CC-based electrodes, respectively. Field–emission scanning electron microscopy (FE–SEM, Nova NanoSEM 230, FEI, Oregon, USA) equipped with an energy dispersive analysis of X-ray (EDAX, Horiba, 7021-H) was used to observe the surface morphologies of the CC-based electrodes.

Photovoltaic performance: Cell efficiencies of the DSSCs with various CC-based electrodes as the counter electrodes were measured by a potentiostat/galvanostat (PGSTAT 30, Autolab, Eco–Chemie, Utrecht, the Netherlands) at AM 1.5G sun light illumination, by using a class A quality solar simulator (XES–301S, AM 1.5G, San–Ei Electric Co., Ltd., Osaka, Japan). An incident light intensity of 100 mW cm^{-2} was applied with a standard Si cell (PECSI01, Peccell Technologies, Inc., Kanagawa, Japan). Incident photon–to–current conversion efficiencies (IPCE) of the DSSCs were recorded by the same potentiostat/galvanostat, under monochromatic light illumination, in a wavelength range of 400-800 nm. To obtain the IPCE data, another class-A solar simulator (PEC–L11, AM1.5G, Peccell Technologies, Inc., Kanagawa, Japan) equipped with a monochromator (model 74100, Oriel Instrument, California, USA) was used. The incident radiation flux (φ) was obtained by using an optical detector (model 818-SL, Newport, California, USA) and a power meter (model 1916-R, Newport, California, USA). The iodide-based electrolyte contains 1.2 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII), 0.035 M iodine (I_2), 0.1 M guanidinium thiocyanate (GuSCN), and 0.5 M 4–tert–butylpyridine (TBP) in acetonitrile/3–methoxypropionitrile (ACN:MPN=8:2 by volume). The cobalt-based electrolyte contains 0.35 M tris(1,10-phenanthroline)cobalt di(bis(trifluoromethane)sulfonimide), 0.05 M tris(1,10-phenanthroline)cobalt tri(bis(trifluoromethane)sulfonimide), 0.8 M TBP, and 0.1 M lithium perchlorate ($LiClO_4$) in acetonitrile. The long-term stability test of the DSSCs with different CEs was performed using another iodide-based electrolyte with binary ionic liquid as the solvent; this electrolyte composed of 0.2 M I_2 and 0.5 M TBP in a mixture of BMII/$EMIBF_4$ (65/35 by volume). The ionic-liquid-based electrolyte penetrated slowly into the gap between the photoanode and CE through the electrolyte-injecting hole, which was previously made onto the counter electrode with a drilling machine, and the hole was sealed with hot-melt glue after the fully filling of the electrolyte.

Electro-catalytic abilities: Cyclic voltammetry (CV) and linear sweep voltammetry were employed to investigate the electro-catalytic abilities of the CC-based electrodes for the reduction of I_3^- to I^- ions. The data of CV were recorded by the same potentiostat/galvanostat mentioned above. A CC-based electrode (with a geometric area of 1 cm^2), a Pt foil, and an Ag/Ag^+ electrode were used as the working, counter, and reference electrodes, respectively. The electrolyte for the CV analysis contained 10.0 mM LiI, 1.0 mM I_2, and 0.1 M $LiClO_4$ in ACN; a scan rate of 100 mV s^{-1} was used. For the long-term cyclic voltammetry analysis, the same three-electrode electrochemical system was performed under a continuous scan for 300 cycles in the iodide-based (10.0 mM LiI, 1.0 mM I_2, and 0.1 M $LiClO_4$ in ACN) and cobalt-based electrolytes (10.0 mM tris(1,10-phenanthroline)cobalt di(bis(trifluoromethane)sulfonimide), 1.0 mM tris(1,10-phenanthroline)cobalt tri(bis(trifluoromethane)sulfonimide), and 0.1 M $LiClO_4$ in ACN). Linear sweep voltammetry was used to obtain Tafel polarization plots for the electrodes; for this purpose the same potentiostat/galvanostat mentioned above and a symmetric cell were employed. The same kind of CC-based electrode was used both for anode and cathode. The electrolyte for this Tafel analysis was composed of 1.2 M DMPII, 0.035 M I_2, 0.1 M GuSCN, and 0.5 M tBP in ACN/MPN (at a volume ratio of 8:2). The scan rate for Tafel analysis was set at 50 mV s^{-1}.

Electrical and impedance properties: Four-point probe analysis and electrochemical impedance spectroscopy (EIS) were used to explore electrical and impedance properties of the electrodes. In the case of four-point probe analysis, electrical conductivity (σ) of an electrode was directly recorded by a Keithley's instrument (Keithley 2400, Keithley Instruments Inc., USA). In the case of EIS analysis, the impdeance data were recorded by the above-mentioned potentiostat/galvanostat, equipped with an FRA2 module, and a symmetric cell with the above-mentioned description was used. The impedance spectra were obtained between 10 mHz to 65 kHz, under the open-circuit condition, with an AC amplitude of ±10 mV. The electrolyte for the EIS analysis was composed of 1.2 M DMPII, 0.035 M I_2, 0.1 M GuSCN, and 0.5 M tBP in ACN/MPN (at a volume ratio of 8:2).

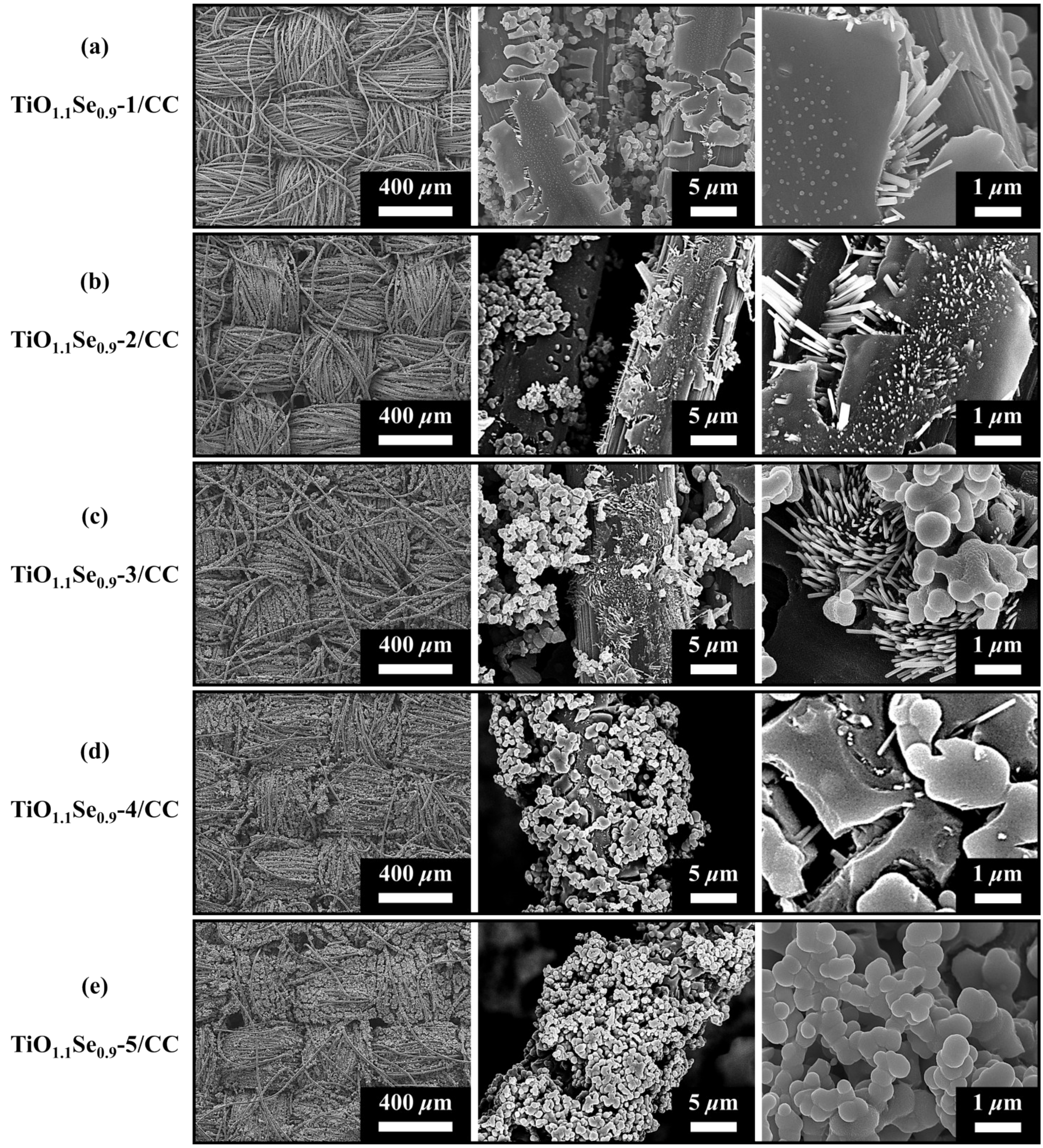

Fig. S1 FE-SEM images of the electrodes of (a) $TiO_{1.1}Se_{0.9}$-1/CC, (b) $TiO_{1.1}Se_{0.9}$-2/CC, (c) $TiO_{1.1}Se_{0.9}$-3/CC, (d) $TiO_{1.1}Se_{0.9}$-4/CC, and (e) $TiO_{1.1}Se_{0.9}$-5/CC, obtained at different resolutions. All images in the first column show carbon cloths covered with different amounts of $TiO_{1.1}Se_{0.9}$; in the second column, owing to higher resolution (5 μm), one to three carbon fibers wrapped with the $TiO_{1.1}Se_{0.9}$ can be seen in the images; in the third column, owing to much higher resolution (1 μm), single CC fibers, wrapped with the $TiO_{1.1}Se_{0.9}$ can be seen in all the images.

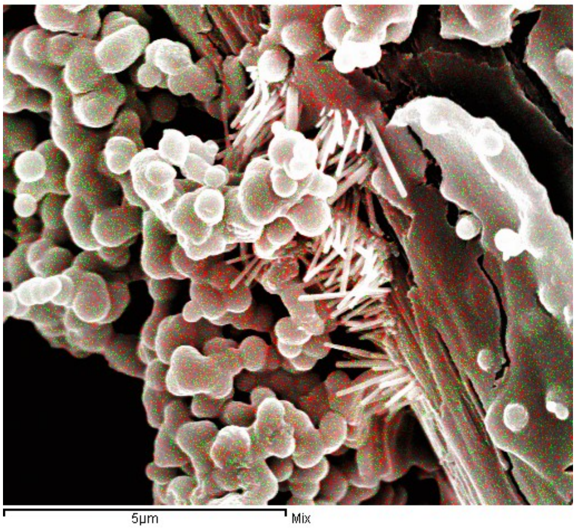

Fig. S2 Elemental distribution map for oxide (green dot) and selenide (red dot) on the synthesized $TiO_{1.1}Se_{0.9}$/CC electrode, measured by an energy dispersive analysis of X-ray (EDAX).

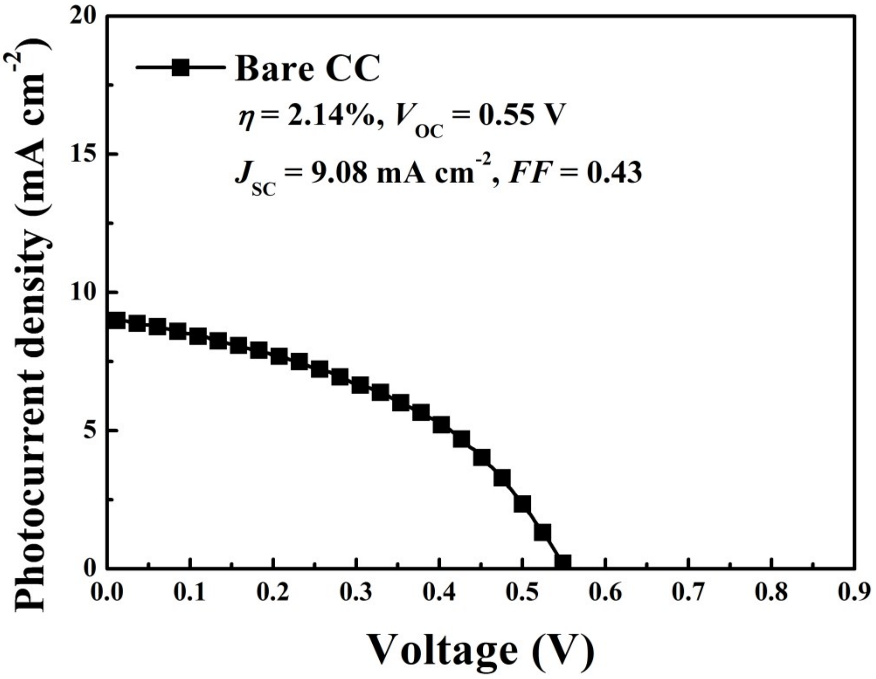

Fig. S3 Photocurrent density–voltage curves of the DSSCs with the counter electrodes of bare CC substrate without loading any catalyst, measured in the cobalt-based electrolyte at 100 mW cm^{-2}.

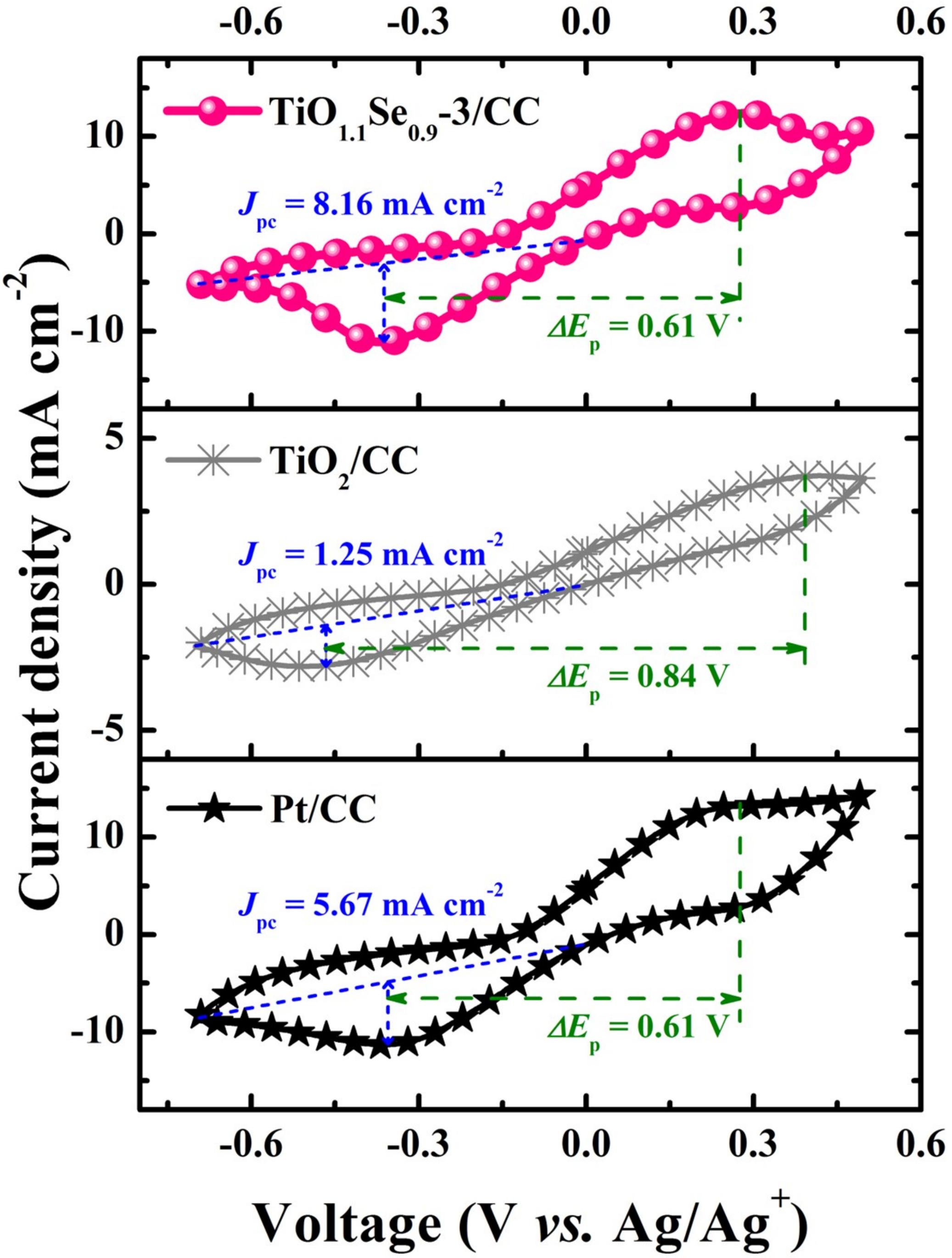

Fig. S4 Cyclic voltammograms of the electrodes of Pt/CC, TiO_2/CC, and $TiO_{1.1}Se_{0.9}$-3/CC. The blue-lined part shows the background curves for the cathodic current peaks, the distance-lines between the peaks and background curves, and the net cathodic peak current density (J_{pc}) values. The green-lined part shows the potential differences between the anodic and cathodic peaks, *i.e.*, the values of the peak-to-peak separation (ΔE_p).

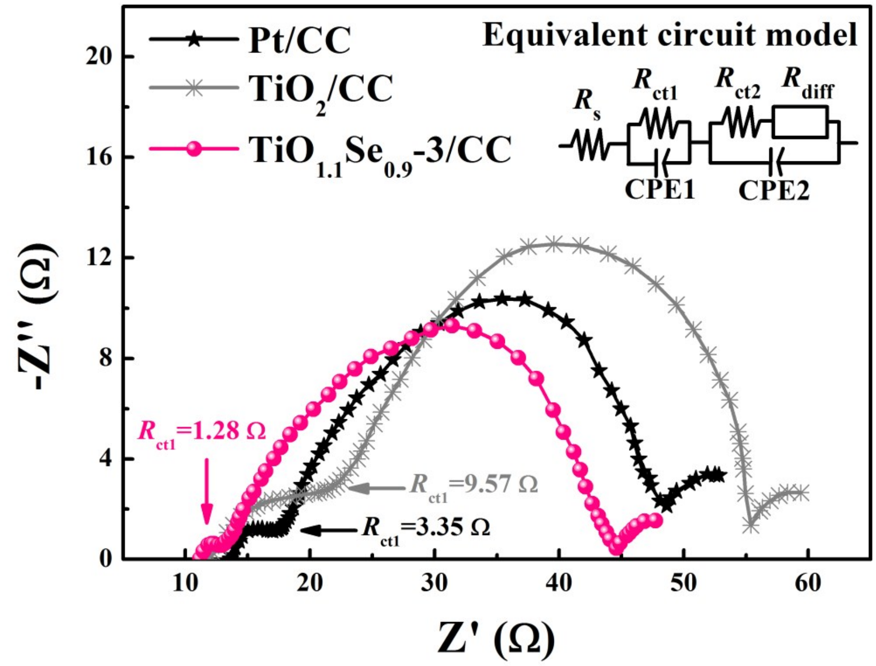

Fig. S5 Electrochemical impedance spectra of the DSSCs with the counter electrodes of Pt/CC, TiO_2/CC, and $TiO_{1.1}Se_{0.9}$-3/CC, measured in the iodide-based electrolyte at 100 mW cm^{-2}.

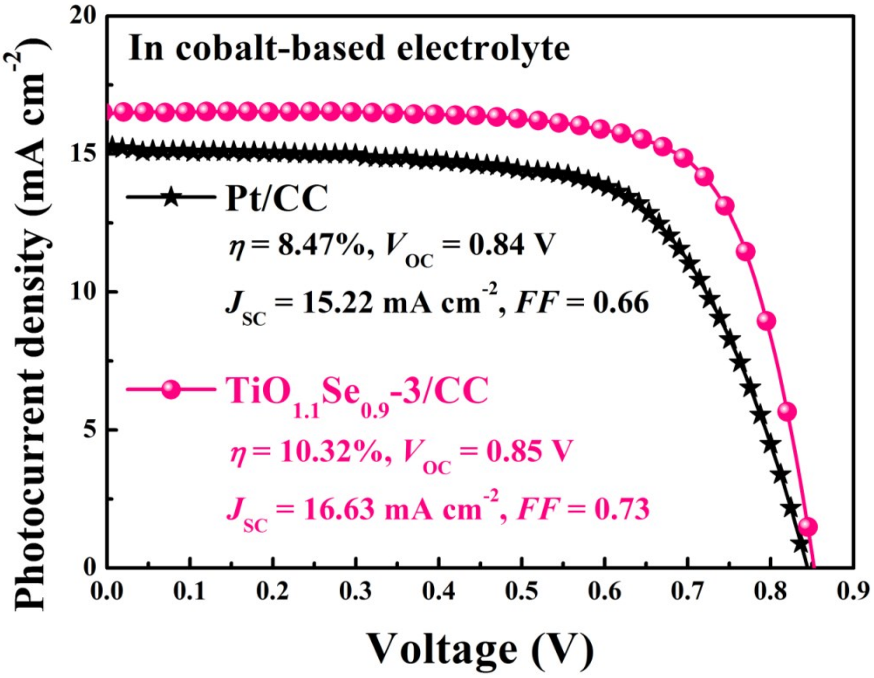

Fig. S6 Photocurrent density–voltage curves of the DSSCs with the counter electrodes of Pt/CC and $TiO_{1.1}Se_{0.9}$-3/CC, measured in the cobalt-based electrolyte at 100 mW cm^{-2}.

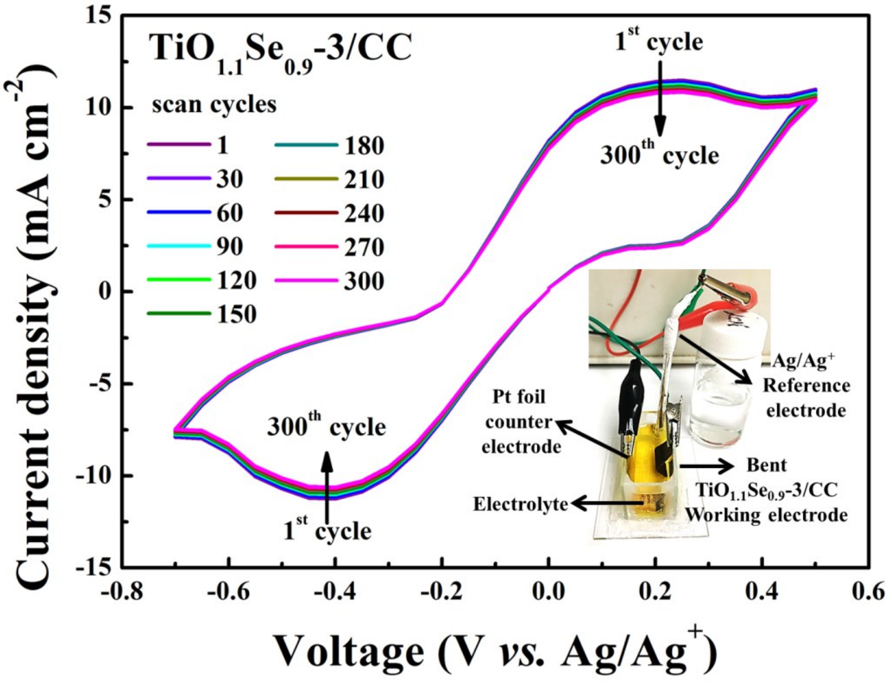

Fig. S7 Long-term cyclic voltammograms for the bent $TiO_{1.1}Se_{0.9}$-3/CC electrode, measured at the continuous 300 cycles of scan in the iodide-based electrolyte.

Table S1 Photovoltaic parameters of the DSSCs with various $TiO_{1.1}Se_{0.9}$/CC counter electrodes, measured in the iodide-based electrolyte at 100 mW cm^{-2}. The integer number in a $TiO_{1.1}Se_{0.9}$/CC electrode represents the number of dip-coating cycles of CC in titanium precursor solution, and thus the larger number means the more amounts of $TiO_{1.1}Se_{0.9}$ materials on the CC substrate. All data were averaged based on three samples.

Counter electrode	η (%)	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF
$TiO_{1.1}Se_{0.9}$-1/CC	7.28±0.13	0.73±0.00	15.68±0.42	0.63±0.01
$TiO_{1.1}Se_{0.9}$-2/CC	8.41±0.04	0.76±0.00	16.81±0.24	0.66±0.01
$TiO_{1.1}Se_{0.9}$-3/CC	9.47±0.25	0.79±0.00	17.22±0.34	0.70±0.00
$TiO_{1.1}Se_{0.9}$-4/CC	8.95±0.02	0.78±0.00	17.00±0.06	0.67±0.00
$TiO_{1.1}Se_{0.9}$-5/CC	8.57±0.08	0.77±0.00	16.83±0.11	0.66±0.00

Table S2 Photovoltaic parameters of the DSSCs with the flexible $TiO_{1.1}Se_{0.9}$-3/CC electrode before and after bending manually for 500 times, measured in the iodide-based or cobalt-based electrolytes at 100 mW cm^{-2}.

Electrolyte	Counter electrode	η (%)	V_{OC} (V)	J_{SC} (mA cm^{-2})	*FF*
Iodide	$TiO_{1.1}Se_{0.9}$-3/CC	9.47±0.25	0.79±0.00	17.22±0.34	0.70±0.00
	Bent $TiO_{1.1}Se_{0.9}$-3/CC	9.29±0.18	0.79±0.00	16.96±0.11	0.70±0.00
Cobalt	$TiO_{1.1}Se_{0.9}$-3/CC	10.32±0.32	0.85±0.00	16.63±0.44	0.73±0.00
	Bent $TiO_{1.1}Se_{0.9}$-3/CC	10.05±0.29	0.85±0.00	16.43±0.23	0.72±0.00