Electronic Supplementary Information

Bi-metallic [Cu/Co(6mna)$_2$]$_n$ metal organic chalcogenolate framework as high-performance electro-catalyst for dye-sensitized solar cells: A ligand-assisted bottom-up synthesis

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1. Materials

Conducting substrate: Fluorine–doped tin oxide (FTO, TEC-7, 7 Ω sq.$^{-1}$) conducting glass was purchased from NSG America, Inc., New Jersey, USA. Carbon cloth (CC, W0S1002, thickness = 0.36 mm, basic 15 weight = 120 g cm^{-2} , sheet resistance = 0.60 Ω sq.$^{-1}$) was bought from CeTech Co., Ltd., Taiwan. *Photoanode:* Titanium (IV) tetraisoproxide (TTIP, > 98%) and 2-methoxyethanol (≥ 99.5%) were obtained from Sigma Aldrich. Titanium (IV) chloride (TiCl$_4$, >99.9%) was obtained from Acros Organics B.V.B.A. Transparent TiO$_2$ paste (TL paste, Ti–nanoxide HT/SP, 20 nm) and surlyn® (SX1170–60, 60 μm) were supplied by Solaronix S.A., Aubonne, Switzerland. Ccommercial light scattering TiO$_2$ particles, ST–41 with an averaged diameter of 200 nm, were obtained from Ishihara Sangyo, Ltd., Japan. Poly(ethylene glycol) (PEG, MW~20,000) were purchased from Merck. Cis-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium (II) bis(tetrabutylammonium) (N719 dye) were supplied by Luminescence Tech. Corp., Taiwan. *Electrolyte:* Lithium iodide (LiI, synthetical grade) and iodine (I$_2$, synthetical grade) were purchased from Merck. 1,2-Dimethyl-3-propylimidazolium iodide (DMPII) was procured from Tokyo Chemical Industry Co., Ltd. Guanidinium thiocyanate (GuSCN, ≥ 99%) and 4-tert-butylpyridine (tBP, 96%) were bought from Acros. Lithium perchlorate (LiClO$_4$, ≥ 98.0%) was obtained from Sigma Aldrich. Tris(1,10-phenanthroline)cobalt(II) bis(trifluoromethanesulfonimide) and tris(1,10-phenanthroline)cobalt(III) tri(trifluoromethanesulfonimide) were synthesized in accordance with our previous studies.[1] Bis(2,9-dimethyl-1,10-phenanthroline)copper(I) trifluoromethanesulfonimide and bis(2,9-dimethyl-1,10-phenanthroline)copper(II) bis(trifluoromethanesulfonimide) were synthesized by a reported procedure.[2] *Solvent:* Acetone (99%) and tert-butyl alcohol (tBA, 96%) were bought from Acros. 3-Methoxypropionitrile (MPN, 99%) was procured from Alfa Aesar. Acetonitrile (MeCN, 99.99%) and dichloromethane (DCM, ≥ 99.8%) were received from J. T. Baker. *N,N*-Dimethylformamide (DMF, ≥ 99.8%), ethanol (EtOH, 99.5%), and isopropyl alcohol (IPA, 99.5%) were obtained from Sigma Aldrich. *MOF synthesis:* Copper (II) nitrate hydrate (Cu(NO$_3$)$_2$·2.5H$_2$O, 98%) was obtained from Honeywell Research Chemicals International Inc., USA. 6,6'-Dithiodinicotinic acid (H$_2$dtdn, >98%) was obtained from Tokyo Chemical Industry Co., Ltd. Pyrazine (Pyz, >99%) was obtained from Thermo Fisher Scientific Inc. 6-Mercaptopyridine-3-carboxylic acid (6mna, >90%) was obtained from Sigma Aldrich. Cobalt (II) chloride hexahydrate (CoCl$_2$·6H$_2$O) and cobalt (II) nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O) were procured from Alfa Aesar.

2. Fabrication of the DSSCs

Conducting substrate, FTO and carbon cloth, were cleaned with a neutral cleaner and then washed with de-ionized water, acetone, and isopropanol sequentially. A mesoporous TiO$_2$ photoanode (with an working area of 0.20 cm^2) was coated on a cleaned FTO by the following procedures. (1) The first TiO$_2$ compact layer (~100 nm) was spin-coated on FTO under 3000 rpm for 30 s using a precursor solution of TTIP/2-methoxyethanol with a weight ratio of 1/3. (2) The second TiO$_2$ transparent layer (~10 μm) was doctor-bladed onto the first layer using the commercial TL paste purchased from Solarnix. (3) The third TiO$_2$ scattering layer (~4 μm) was doctor-bladed onto the second layer using a reported home-made paste[1]. (4) Last, the TiO$_2$ thin film was treated by a 70 mM of TiCl$_4$ solution

(with a solvent) at 70 °C for 30 min in a mixing solvent of deionc water/ethanol (v/v=9/1). The TiO_2 layer made by every step would be followed by a sintering process at 500 °C for 30 min in an ambient atmosphere. After the sintering process, the TiO_2 photoanode was immersed in a $5.0×10^{-4}$ M of N719 dye solution using a mixed solvent of MeCN/tBA with a volume ratio of 1:1 at room temperature for 24 h. A TiO_2 photoanode was coupled with a counter electrode made by this work. And the cell gap was maintained by using a 60 μm-thick Surlyn® film as the spacer.

3.   Material characterizations

Crystallinity and molecular structure of as-synthesized MOF particle were analyzed by powder X-ray diffraction pattern spectroscopy (PXRD, Bruker D8 advance, Billerica, USA) and single crystal X-ray diffraction pattern spectroscopy (SCXRD, Bruker D8 venture, Billerica, USA). Nitrogen-gas (N_2) adsorption-desorption isotherms for various MOF powders were investigated by Micromeritics 3Flex Adsorption Analyzer Georgia USA. Film morphology was observed by field–emission scanning electron microscopy (FE–SEM, Nova NanoSEM 230, FEI, Oregon, USA).

4.   Photovoltaic performance measurement

Photovoltaic parameters of the DSSCs with different counter electrodes were obtained by a potentiostat/galvanostat (Metrohm Autolab PGSTAT204, Autolab, Eco-Chemie, the Netherlands) at the simulated solar irradiation (100 mW cm^{-2}; AM 1.5G) and Philip desk lamp (Helix 23WD EMI lamp; a correlated color temperature of 6500K; 6, 3, and 1 klux). The simulated solar irradiation was performed by a class A quality solar simulator (PEC–L11, AM1.5G, Peccell Technologies, Inc., Kanagawa, Japan). The incident light intensity was calibrated by a standard Si cell (PECSI01, Peccell Technologies, Inc.) and by an optical detector (model 818-SL, Newport, California, USA) coupled with a power meter (model 1916-R, Newport, California, USA). The DSSC device was composed of a sandwitch structure of photoanode/ electrolyte/ counter electrode; where an indentical TiO_2 film adsorbed with N719 sensitizer was the photoanode, an liquid iodide-based mixture was the electrolyte, and the different electrodes made by this work were used as the counter electrodes. Here, the iodide-based electrolyte contained 1.2 M DMPII, 0.035 M I_2, 0.1 M GuSCN, and 0.5 M tBP in MPN/MeCN (volume ratio of 1:4) and was injected into the gap between photoanode and counter electrode by capillarity.

5.   Cyclic voltammetry (CV) analysis

CV analysis was executed by a potentiostat/galvanostat (Metrohm Autolab PGSTAT204, Autolab, Eco-Chemie, the Netherlands) using a three–electrode system. The sample electrode was used as the working electrode. A Pt foil and Ag/Ag$^+$ electrode were used as the auxiliary and reference electrodes, respectively. For the measurements of I^-/I_3^- redox mediator, the iodide-based electrolyte contained 10.0 mM of LiI, 1.0 mM of I_2, and 0.1 M of $LiClO_4$ in acetonitrile. For the measurements of Co-phen^{2+}/Co-phen^{3+} redox mediator, the cobalt-based electrolyte contained 10.0 mM of tris(1,10-phenanthroline)cobalt(II) bis(trifluoromethanesulfonimide), 1.0 mM of tris(1,10-phenanthroline)-cobalt(III) tri(trifluoromethanesulfonimide), and 0.1 M $LiClO_4$ in acetonitrile. For the measurements

of Cu-dmp$^+$/Cu-dmp^{2+} redox mediator, the copper-based electrolyte contained 10.0 mM of bis(2,9-dimethyl-1,10-phenanthroline)copper(I) trifluoromethanesulfonimide, 1.0 mM of bis(2,9-dimethyl-1,10-phenanthroline)copper(II) bis(trifluoromethanesulfonimide), and 0.1 M of LiClO$_4$ in acetonitrile. The scan rate for CV analysis was performed at 20, 40, 60, 80, or 100 mV s^{-1}.

6.   Tafel polarization plot, and electrochemical impedance spectra

Tafel polarization plots and electrochemical impedance spectra (EIS) analysese were recorded a potentiostat/galvanostat (Metrohm Autolab PGSTAT204, Autolab, Eco-Chemie, the Netherlands) equipped with a FRA2 module by using a symmetrical cell structure of electrode/electrolyte/electrode; where an electrode made by this work was applied for both anode and cathode. The electrolyte for Tafel and EIS analyses contained 1.2 M DMPII, 0.035 M I$_2$, 0.1 M GuSCN, and 0.5 M tBP in MPN/MeCN (volume ratio of 1:4). For Tafel measurement, linear sweep voltammetry (LSV) was performed from 1 V to –1 V at a DC bias with a scan rate of 100 mV s^{-1}. A Tafel polarization curve is presented as a logarithm of current density–voltage (log J–V) curve, which is generally divided into three zones: (1) the polarization zone for forming an electrical double layer at $|V| < 120$ mV, (2) the Tafel zone for executing charge transfer at 120 mV $< |V| < 400$ mV, and (3) the diffusion zone for reaching a horizontal limiting current at $|V| > 400$ mV. Accordingly, a linear fitting line is obtained at the anodic or cathodic Tafel zone to find the exchanged current density (J_0; mA cm^{-2}) at the intercept (at $V = 0$). In a region of log $|J_0|\pm 0.2$ mA cm^{-2}, a Tafel slope (β; mV decade^{-1}) for each sample is acquired by another linear fitting line, which is commonly presented as a voltage–logarithm of current density (V–log J) curve.

For EIS analysis, the data was collected using the same dummy cell as for Tafel analysis under an AC amplitude of ± 10 mV, an AC frequency from 1 Hz to 100 kHz, and an applied bias of 0 V. A Nyquist plot is presented as the imaginary impedance–real impedance (-Z''–Z') spectra, which is typically divided into three regions: (1) high-frequency region of $10^5 \sim 10^4$ Hz at the left-hand-side onset point, referring to the series resistance (R_s) at the electro-catalytic film/substrate interface; (2) middle-frequency region of $10^4 \sim 10^3$ Hz for collecting the radius of the left-hand-side semi-circle, referring to the charge transfer resistance (R_{ct}) at the electro-catalytic film/electrolyte interface; (3) low-frequency region of $10^3 \sim 10^0$ Hz for getting the diameter of right-hand-side semi-circle, referring to Warburg diffusion resistance (Z_W) within the electrolyte layer.

Table S1 A partial list of the DSSC performance with MOF-based counter electrodes, based on the device using a photoanode of TiO_2/N719 and an I^-/I_3^- electrolyte.

Ligands	Counter Electrode	η [%]	η of Pt [%]	Ref.
Imidazole	FTO/ZIF-67/ethyl cellulose	2.9	7.9	[3]
	FTO/ZIF-67 derived CoS_2/carbon nanocage	8.2		
	FTO/ZIF-67 derived $CoTe_2$/N-doped CNT-grafted polyhedron	9.0	8.0	[4]
	FTO/ZIF-67 derived $CoTe_2$/N-doped graphitic carbon-coated polyhedron	8.6		
	FTO/ZIF-67 derived Co-doped MoS_x hollow nanobox	9.6	8.4	[5]
	FTO/ ZIF-67 derived $CoSe_2$/N-doped CNT	9.3	7.8	[6]
	FTO/(ZIF-8/ZIF-67) derived Ni/Co-embedded N-doped carbon polyhedron/CNT	8.8	7.3	[7]
	FTO/ZIF-8/PEDOT:PSS	7.0	7.2	[8]
	FTO/ZIF-8/PEDOT:PSS	5.7	8.5	[9]
	FTO/(ZIF-8@SiO_2) derived yolk-shell (N-doped carbon@SiO_2)/PEDOT:PSS	10.0		
	FTO/ZIF-8 derived N-doped carbon	8.3	8.9	[10]
	FTO/(ZIF-8@polydopamine) derived N-doped carbon	9.0		
	FTO/ZIF-7/PEDOT:PSS	5.3	8.3	[11]
	FTO/ZIF-7 derived ZnSe/N-doped carbon cube/PEDOT:PSS	8.7		
BDC (or BTC)	FTO/Co-BDC derived $CoSe_2$ (spin-coated)	6.9	6.4	[12]
	FTO/Co-BDC derived $CoSe_2$ (bottom-up grown)	5.8		
	FTO/Zn-BTC derived ZnO-doped carbon	7.7	9.4	[13]
	FTO/(Co-BTC/Ni-BTC) derived cardon decorated Co/Ni alloy	9.3	8.0	[14]
TCPP	FTO/Co-TCPP derived $CoS_{1.097}$@N-doped carbon	9.1	8.0	[15]
	CC/Zr-TCPP/s-PT	8.9	8.2	[16]
	FTO/annealed Zn-TCPP	5.6	6.7	[17]
Mercaptonicotinate	FTO/[Cu_2(6mna)(6mn)NH_4]$_n$/PEDOT	8.3	7.7	[18]
	CC/[Cu_2(6mna)(6mn)NH_4]$_n$/PEDOT	9.5	N.A.	
	CC/[Cu_2(6mna)(6mn)NH_4]$_n$-NO_3	9.4	9.3	This work
	CC/[Co_2(6mna)$_2$]$_n$-NO_3	9.4		
	CC/[Co_2(6mna)$_2$]$_n$-Cl	9.9		
	CC/[Cu/Co(6mna)$_2$]$_n$-NO_3	9.8		
	CC/[Cu/Co(6mna)$_2$]$_n$-Cl	10.0		

CNT= carbon nanotube; PEDOT= poly(3,4-ethylenedioxythio-phene); PEDOT:PSS= poly(3,4-ethylenedioxythio-phene): poly(styrene-sulfonate); s-PT= sulfonated-poly(thiophene-3-[2-(2-methoxyethoxy) ethoxy]-2,5-diyl); 6mna= 6-mercaptonicotinic acid; 6mn= 6-mercaptonicotinate.
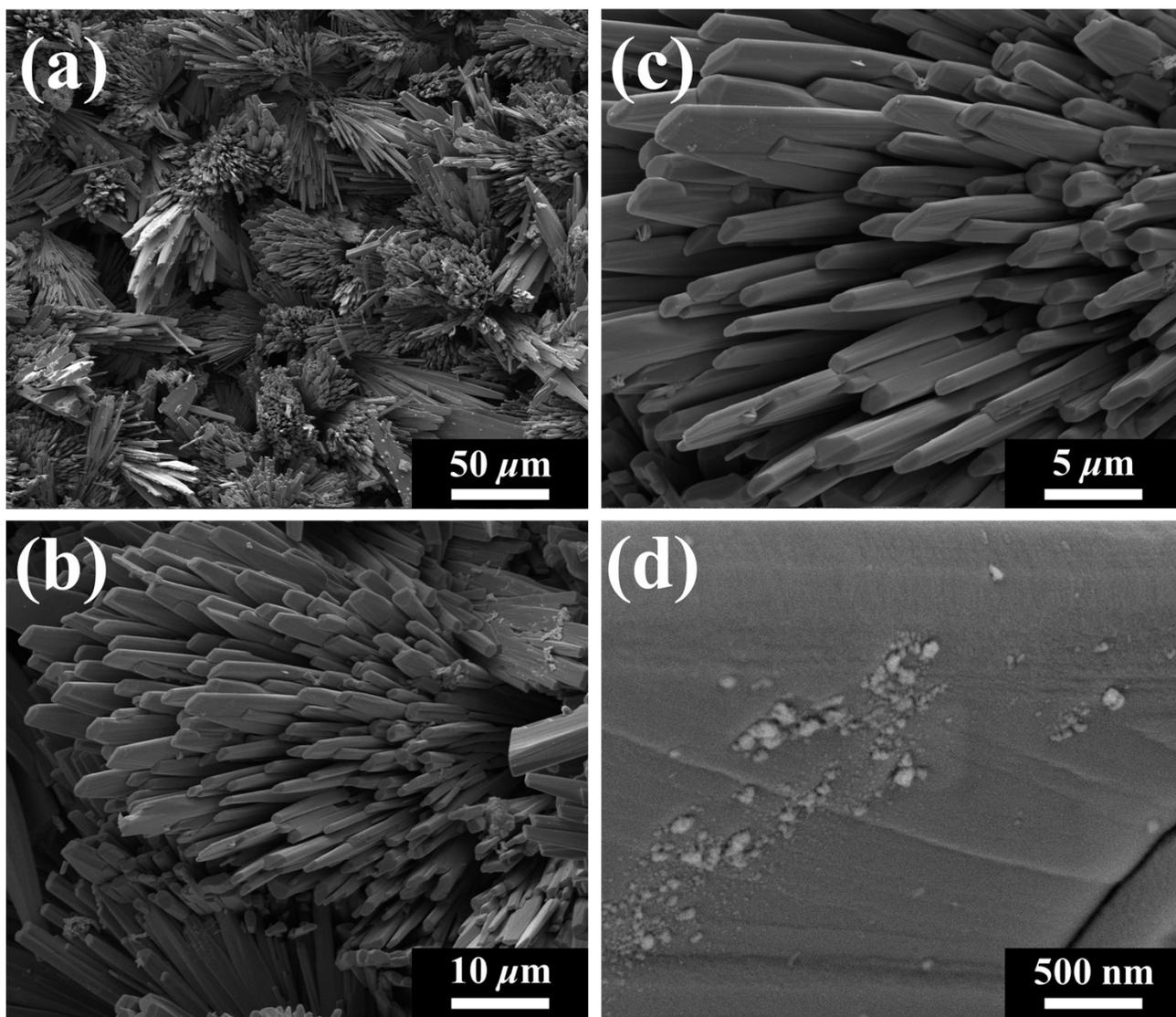
Fig. S1   FE-SEM images of the CC/[Cu$_2$(6mna)(6mn)NH$_4$]$_n$-NO$_3$ electrode synthesized by 72 h, recorded at the magnification of (a) 1 k, (b) 5 k, (c) 10 k, and (d) 100 k.
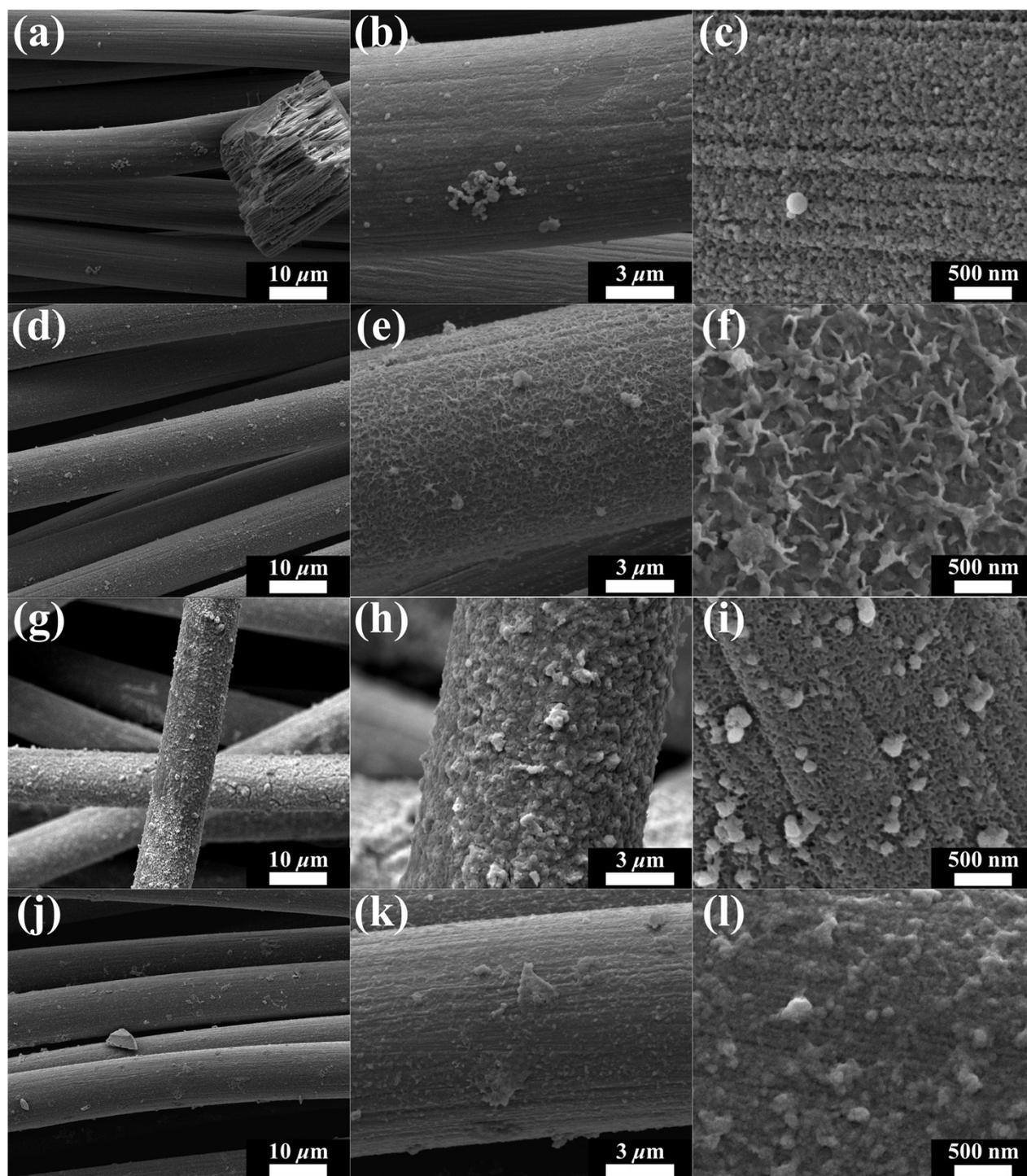
Fig. S2 FE-SEM images of various CC/[Co$_2$(6mna)$_2$]$_n$-NO$_3$ electrodes, synthesized by the reaction time of (a-c) 20, (d-f) 48, (g-i) 72, and (j-l) 96 h.
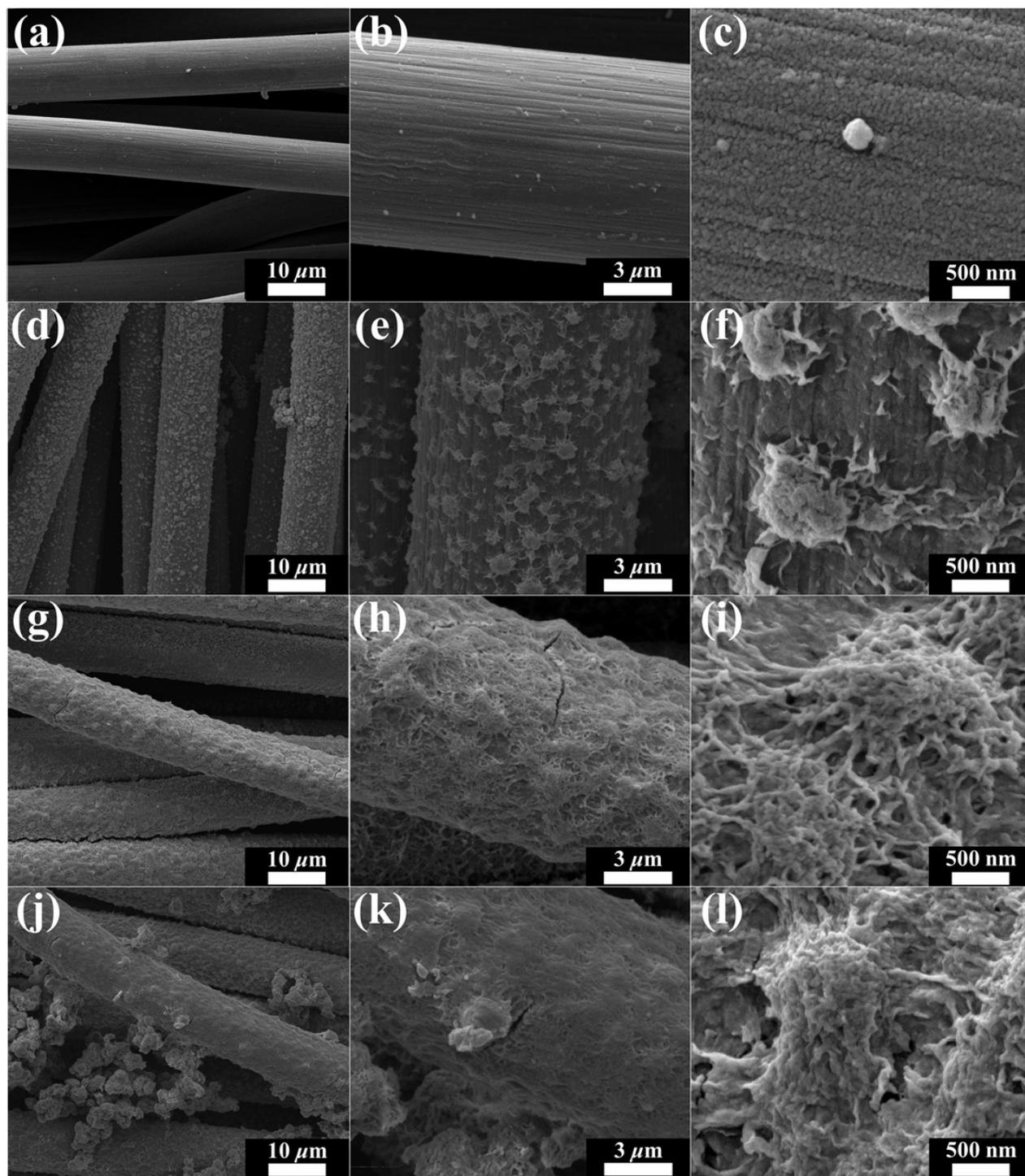
Fig. S3 FE-SEM images of various CC/[Co$_2$(6-mna)$_2$]$_n$-Cl electrodes, synthesized by the reaction time of (a-c) 20, (d-f) 48, (g-i) 72, and (j-l) 96 h.

Fig. S4 FE-SEM images of the CC/[Cu/Co(6mna)$_2$]$_n$-NO$_3$ electrode synthesized by 72 h, recorded at the magnification of (a) 1 k, (b) 5 k, (c) 10 k, and (d) 100 k.

(a) Spectrum 2

Element	Weight%	Atomic%
C K	57.25	73.80
N K	4.44	4.91
O K	14.07	13.61
S K	6.36	3.07
Co L	13.47	3.54
Cu L	4.41	1.07
Totals	100.00	

Full Scale 2549 cts Cursor: 0.000

(b) Spectrum 1

Element	Weight%	Atomic%
C K	31.57	52.20
N K	6.95	9.85
O K	16.78	20.83
S K	8.99	5.57
Co L	15.98	5.39
Cu L	19.73	6.17
Totals	100.00	

Full Scale 2549 cts Cursor: 0.000

(c) Spectrum 1

Element	Weight%	Atomic%
C K	16.80	34.59
N K	3.38	5.97
O K	19.61	30.32
S K	13.02	10.04
Co L	23.37	9.81
Cu L	23.82	9.27
Totals	100.00	

Full Scale 2549 cts Cursor: 0.000

(d) Spectrum 1

Element	Weight%	Atomic%
C K	52.16	71.21
N K	2.69	3.15
O K	14.90	15.27
S K	8.97	4.59
Co L	14.19	3.95
Cu L	7.08	1.83
Totals	100.00	

Full Scale 2549 cts Cursor: 0.000

Fig. S5 EDAX spectra of the CC/[Cu/Co(6mna)$_2$]$_n$-NO$_3$ electrode synthesized by 72 h, recorded at (a) silk-like particles, (b) sharp octahedrons, (c) irregular chunks, and (d) bulk film.

Fig. S6   FE-SEM images of the CC/[Cu/Co(6mna)$_2$]$_n$-Cl electrode synthesized by 72 h, recorded at the magnification of (a) 1 k, (b) 5 k, (c) 10 k, and (d) 100 k.

(a)

Spectrum 3		
Element	Weight%	Atomic%
C K	65.17	79.32
N K	3.11	3.25
O K	12.69	11.60
S K	5.48	2.50
Co L	12.14	3.01
Cu L	1.39	0.32
Totals	100.00	

Full Scale 2549 cts Cursor: 0.000

(b)

Spectrum 2		
Element	Weight%	Atomic%
C K	20.39	45.03
N K	3.65	6.91
O K	8.34	13.83
S K	13.60	11.25
Co L	13.15	5.92
Cu L	40.87	17.06
Totals	100.00	

Full Scale 2549 cts Cursor: 0.000

(c)

Spectrum 1		
Element	Weight%	Atomic%
C K	25.15	47.07
N K	2.20	3.53
O K	17.54	24.65
S K	13.38	9.38
Co L	22.00	8.39
Cu L	19.73	6.98
Totals	100.00	

Full Scale 2549 cts Cursor: 0.000

(d)

Spectrum 1		
Element	Weight%	Atomic%
C K	62.86	78.60
N K	2.65	2.84
O K	12.12	11.38
S K	7.20	3.37
Co L	12.43	3.17
Cu L	2.75	0.65
Totals	100.00	

Full Scale 2549 cts Cursor: 0.000

Fig. S7 EDAX spectra of the CC/[Cu/Co(6mna)$_2$]$_n$-Cl electrode synthesized by 72 h, recorded at (a) flower-like particles, (b) spherical particles, (c) irregular aggregations, and (d) bulk film.
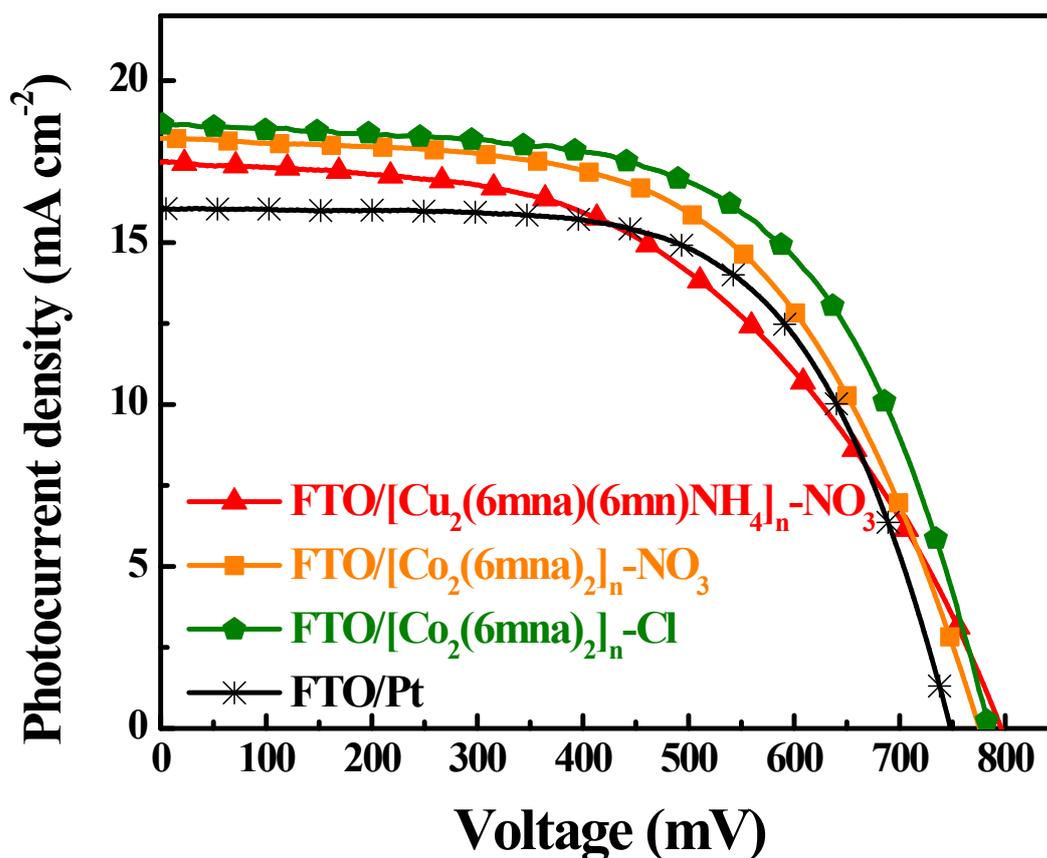
Fig. S8   Photocurrent density–voltage curves of DSSCs coupled with various counter electrodes of FTO/[Cu$_2$(6mna)(6mn)NH$_4$]$_n$-NO$_3$, CC/[Co$_2$(6mna)$_2$]$_n$-NO$_3$, FTO/[Cu/Co(6mna)$_2$]$_n$-NO$_3$, and FTO/Pt, measured at a simulated AM 1.5G solar illumination (100 mW cm^{-2}, AM 1.5G).

Table S2   Photovoltaic parameters of DSSCs coupled with various counter electrodes of FTO/[Cu$_2$(6mna)(6mn)NH$_4$]$_n$-NO$_3$, CC/[Co$_2$(6mna)$_2$]$_n$-NO$_3$, FTO/[Cu/Co(6mna)$_2$]$_n$-NO$_3$, and FTO/Pt. The standard deviation data for each sample is measured at the simulated solar irradiation (100 mW cm^{-2}, AM 1.5G) using ten independent devices.

Electrode	η (%)	V_{OC} (mV)	J_{SC} (mA cm^{-2})	*FF*
FTO/[Cu$_2$(6mna)(6mn)NH$_4$]$_n$-NO$_3$	7.1 ± 0.4	800 ±90	17.3 ± 0.4	0.52 ± 0.02
FTO/[Co$_2$(6mna)$_2$]$_n$-NO3	8.1 ± 0.1	780 ±10	18.2 ± 0.2	0.58 ± 0.01
FTO/[Co$_2$(6mna)$_2$]$_n$-Cl	8.8 ± 0.3	780 ±120	18.6 ± 0.3	0.61 ± 0.01
FTO/Pt	7.7 ± 0.0	750 ±20	16.1 ± 0.1	0.64 ± 0.01
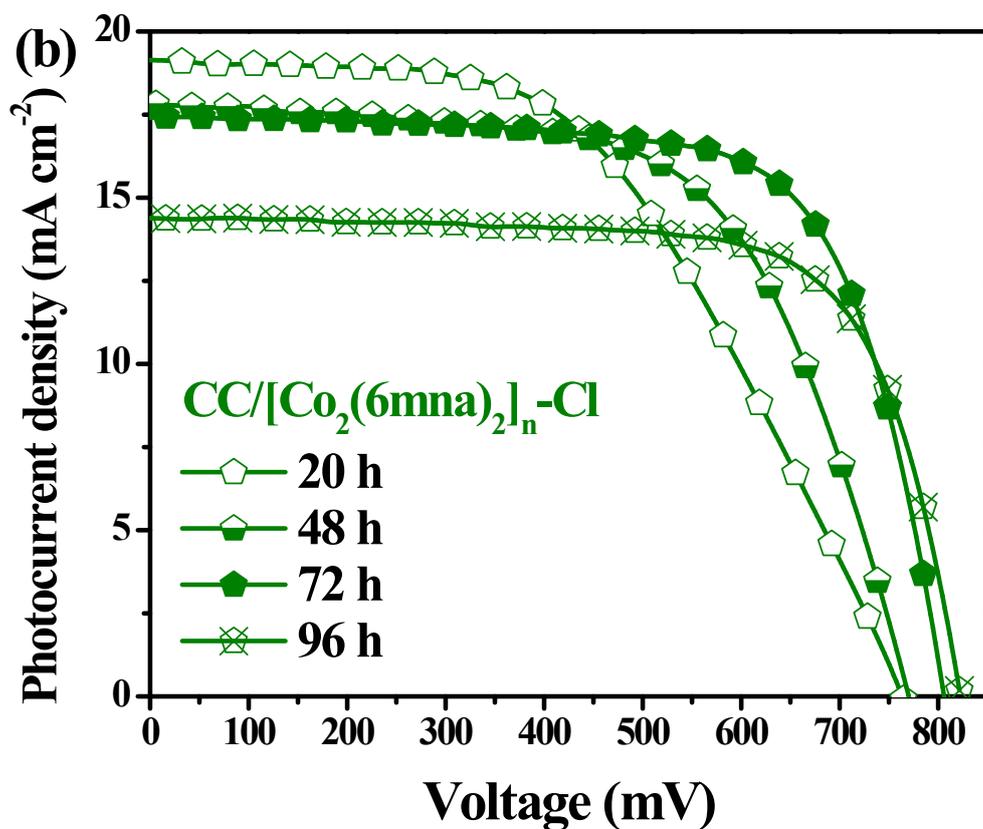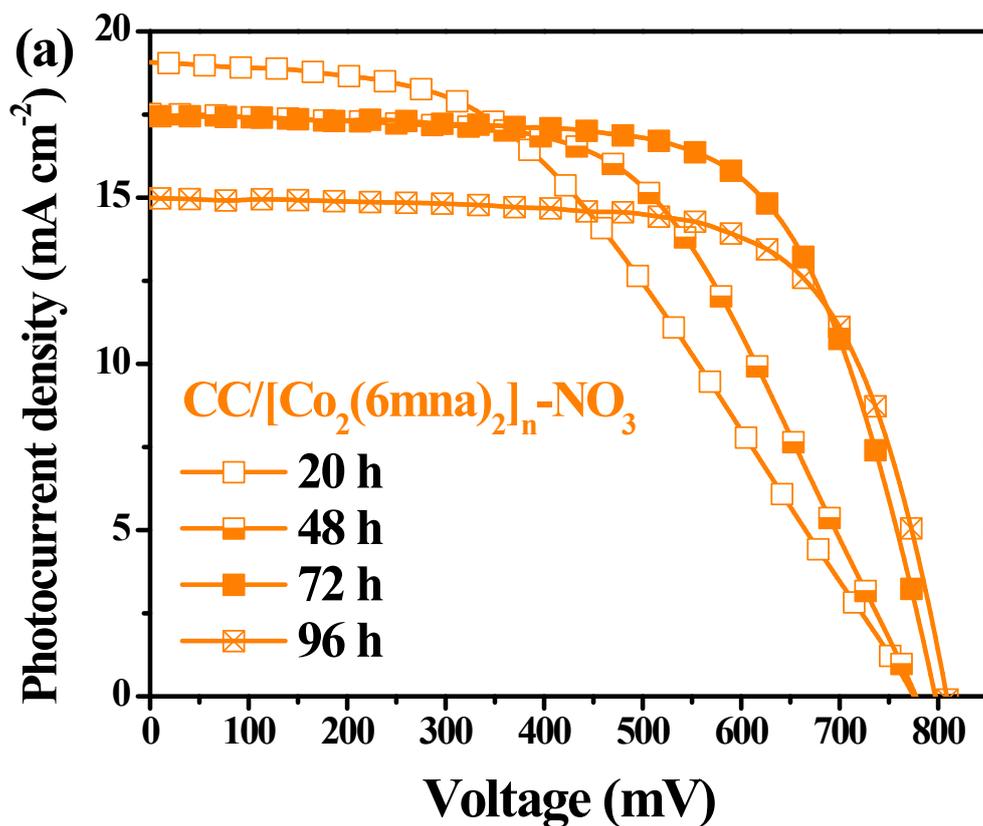
Fig. S9 Photocurrent density–voltage curves of DSSCs coupled with the counter electrodes of (a) various CC/$[Co_2(6mna)_2]_n$-NO_3 and (b) various CC/$[Co_2(6mna)_2]_n$-Cl, synthesized by different reaction times (20, 48, 72, and 96 h).

Table S3 Photovoltaic parameters of DSSCs coupled with the counter electrodes of various $CC/[Co_2(6mna)_2]_n$-NO_3 and $CC/[Co_2(6mna)_2]_n$-Cl, synthesized by different reaction times.

Electrode	Reaction time (h)	η (%)	V_{OC} (mV)	J_{SC} (mA cm^{-2})	FF
$CC/[Co_2(6mna)_2]_n$-NO_3	20	6.5 ± 0.2	770 ±130	19.0 ± 0.3	0.44 ± 0.00
	48	7.8 ± 0.1	780 ±140	17.6 ± 0.4	0.57 ± 0.02
	72	9.4 ± 0.1	800 ±20	17.4 ± 0.1	0.68 ± 0.00
	96	8.6 ± 0.4	810 ±140	15.1 ± 0.6	0.70 ± 0.00
$CC/[Co_2(6mna)_2]_n$-Cl	20	7.5 ± 0.3	760 ±150	19.0 ± 0.3	0.52 ± 0.01
	48	8.5 ± 0.3	770 ±140	17.9 ± 0.5	0.62 ± 0.01
	72	9.9 ± 0.3	800 ±50	17.5 ± 0.5	0.71 ± 0.01
	96	8.6 ± 0.5	820 ±90	14.5 ± 0.7	0.72 ± 0.00

Table S4 Photovoltaic parameters of the DSSCs coupled with the $CC/[Cu/Co(6mna)_2]_n$-Cl counter electrodes, measured by a Philip desk lamp (Helix 23WD EMI) illumination at 0.5, 1.0, 3.0, and 6.0 klux. The standard deviation for each data is based on five independent devices.

Irradiance (mW cm^{-2})	η (%)	V_{OC} (mV)	J_{SC} (mA cm^{-2})	FF
0.16 (0.5 klux)	12.2 ± 0.1	580 ±10	0.05 ± 0.00	0.66 ± 0.01
0.32 (1.0 klux)	19.5 ± 0.1	620 ± 0	0.15 ± 0.00	0.66 ± 0.00
0.97 (3.0 klux)	23.3 ± 0.1	660 ±10	0.51 ± 0.00	0.67 ± 0.00
1.95 (6.0 klux)	26.4 ± 0.3	680 ±10	1.14 ± 0.02	0.66 ± 0.01

Table S5 Electrochemical properties of the electrodes of $CC/[Cu/Co(6mna)_2]_n$-NO_3, $CC/[Cu/Co(6mna)_2]_n$-Cl, and CC/Pt in an iodide-based electrolyte at a scan rate of 10 mV s^{-1}.

Electrode	J_{pc} [mA cm^{-2}]	E_{sep} [mV]
$CC/[Cu/Co(6mna)_2]_n$-NO_3	0.9	417
$CC/[Cu/Co(6mna)_2]_n$-Cl	1.2	306
CC/Pt	0.8	474
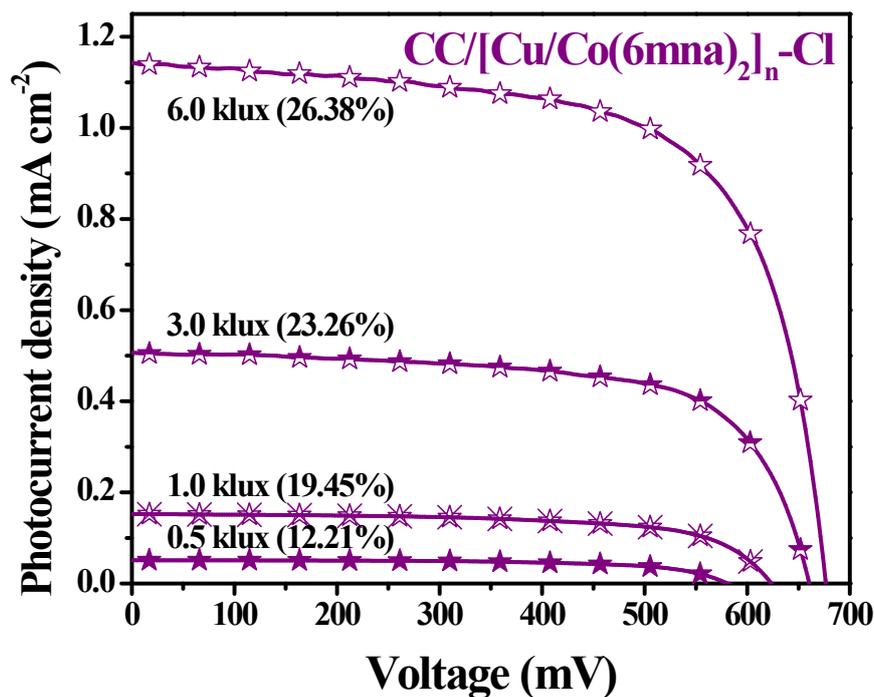
Fig. S10   Photocurrent density–voltage curves of the DSSCs coupled the optimal CC/[Cu/Co(6mna)$_2$]$_n$-Cl counter electrodes, measured at room light illumination (Philips TL5, 14W, 6500K).
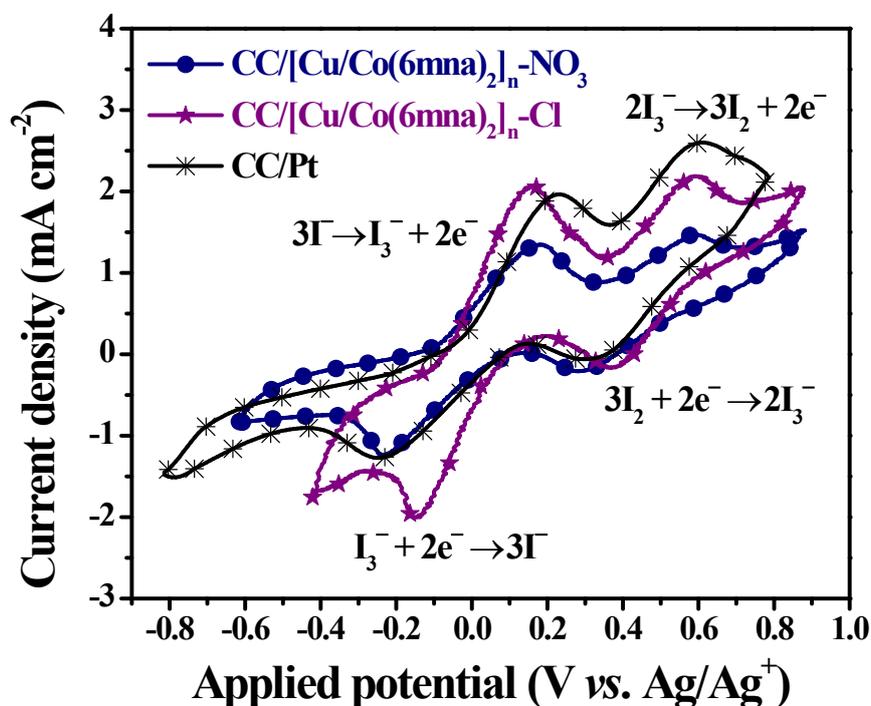
Fig. S11   Cyclic voltammograms of CC/[Cu/Co(6mna)$_2$]$_n$-NO$_3$, CC/[Cu/Co(6mna)$_2$]$_n$-Cl, and CC/Pt electrodes, measured in an iodide-based electrolyte at a scan rate of 10 mV s^{-1}.
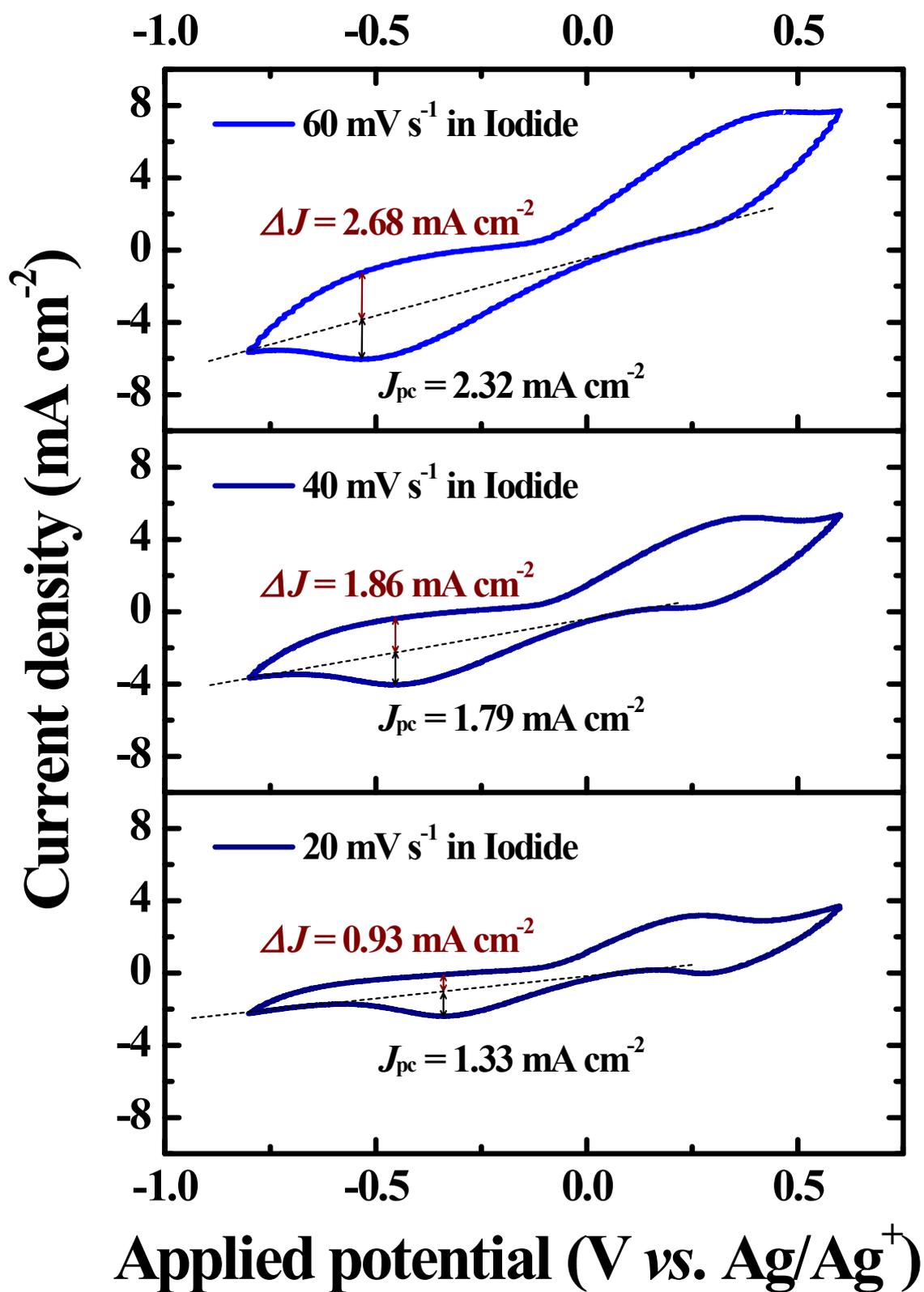
Fig. S12 Cyclic voltammograms of CC/[Cu/Co(6mna)$_2$]$_n$-Cl electrode, measured in an iodide-based electrolyte at various scan rates (20, 40, and 60 mV s^{-1}).
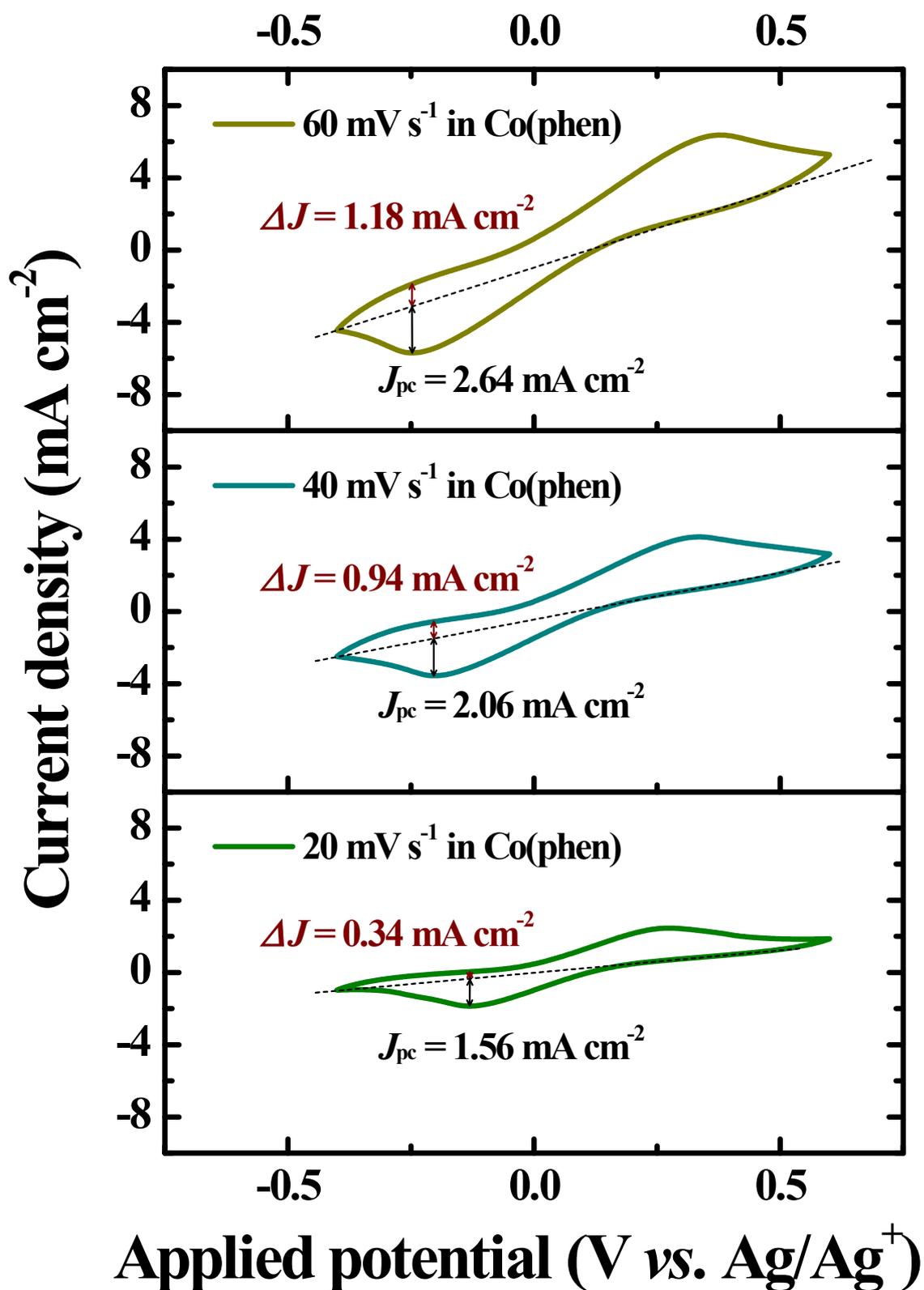
Fig. S13 Cyclic voltammograms of CC/[Cu/Co(6mna)$_2$]$_n$-Cl electrode, measured in an Co(phen)-based electrolyte at various scan rates (20, 40, and 60 mV s^{-1}).
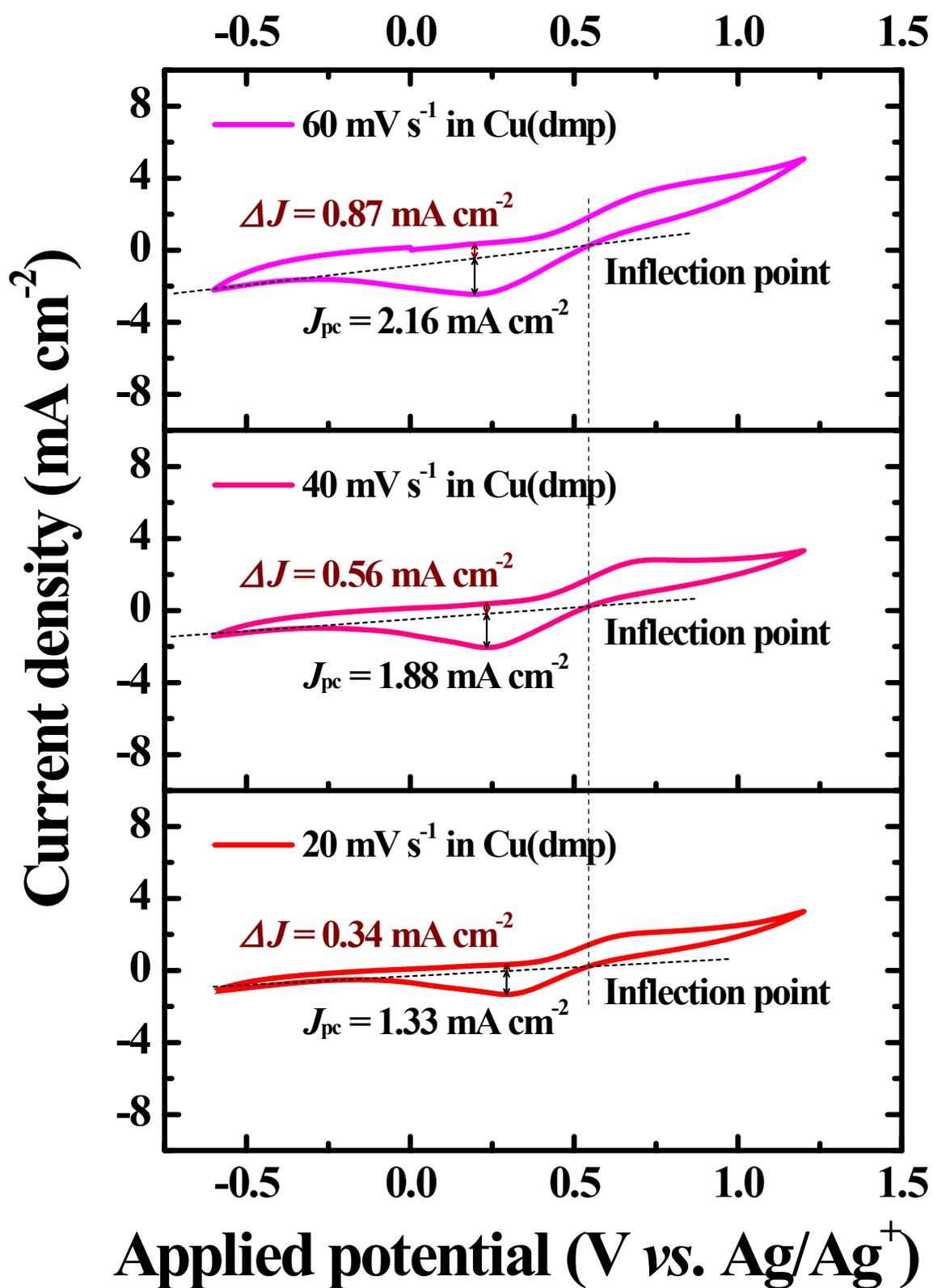
Fig. S14 Cyclic voltammograms of CC/[Cu/Co(6mna)₂]ₙ-Cl electrode, measured in an Cu(dmp)-based electrolyte at various scan rates (20, 40, and 60 mV s⁻¹).
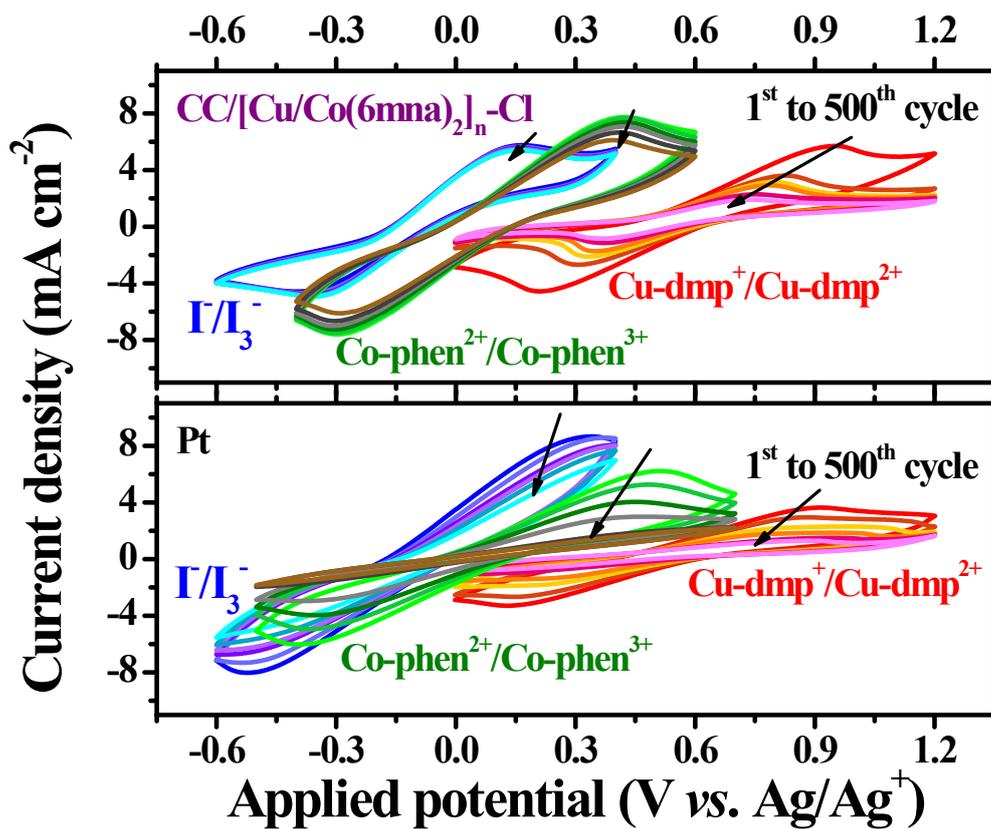
Fig. S15 Long-term cyclic voltammograms of the CC/[Cu/Co(6mna)$_2$]$_n$-Cl and CC/Pt electrodes, measured at 100 mV s^{-1} in an iodide-based (blue), cobalt-based (green), or copper-based (red) electrolytes.
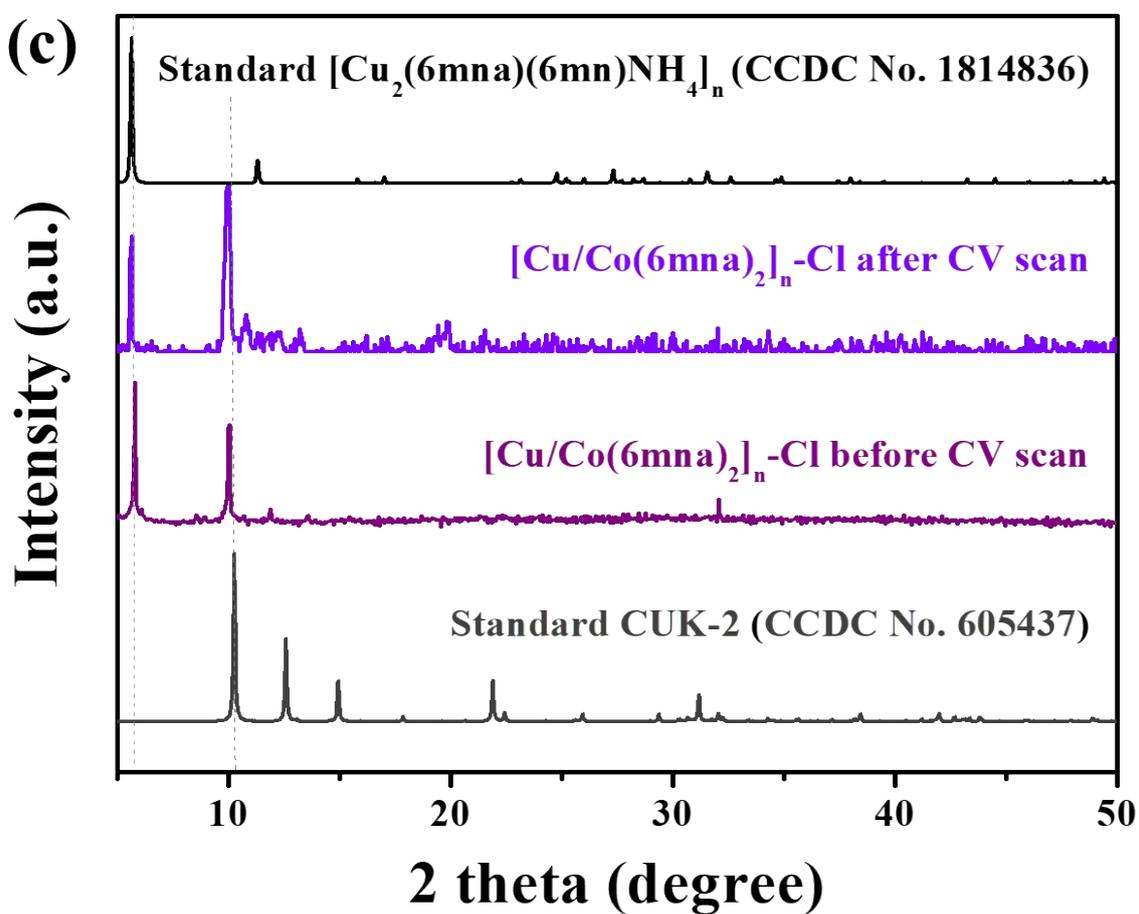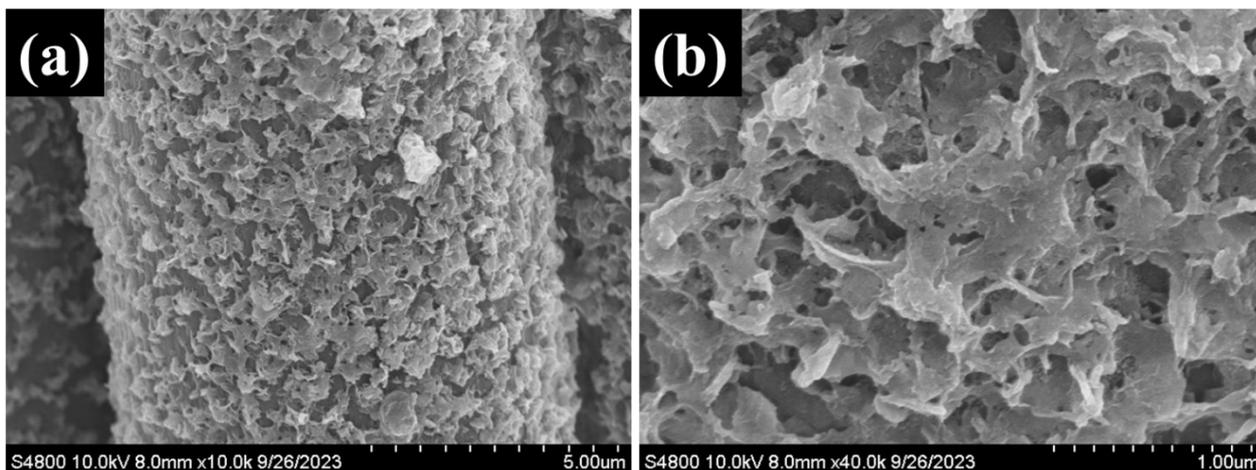
Fig. S16 FE-SEM images of the CC/[Cu/Co(6mna)$_2$]$_n$-Cl electrode synthesized by 72 h, recorded after 500 cycles of CV scanning at the magnification of (a) 10 k and (b) 40 k. (c) Powder X-ray diffraction patterns of [Cu/Co-(6mna)$_2$]$_n$-Cl before (purple line) and after (violet line) long-term CV scan in I$^-$/I$_3^-$.
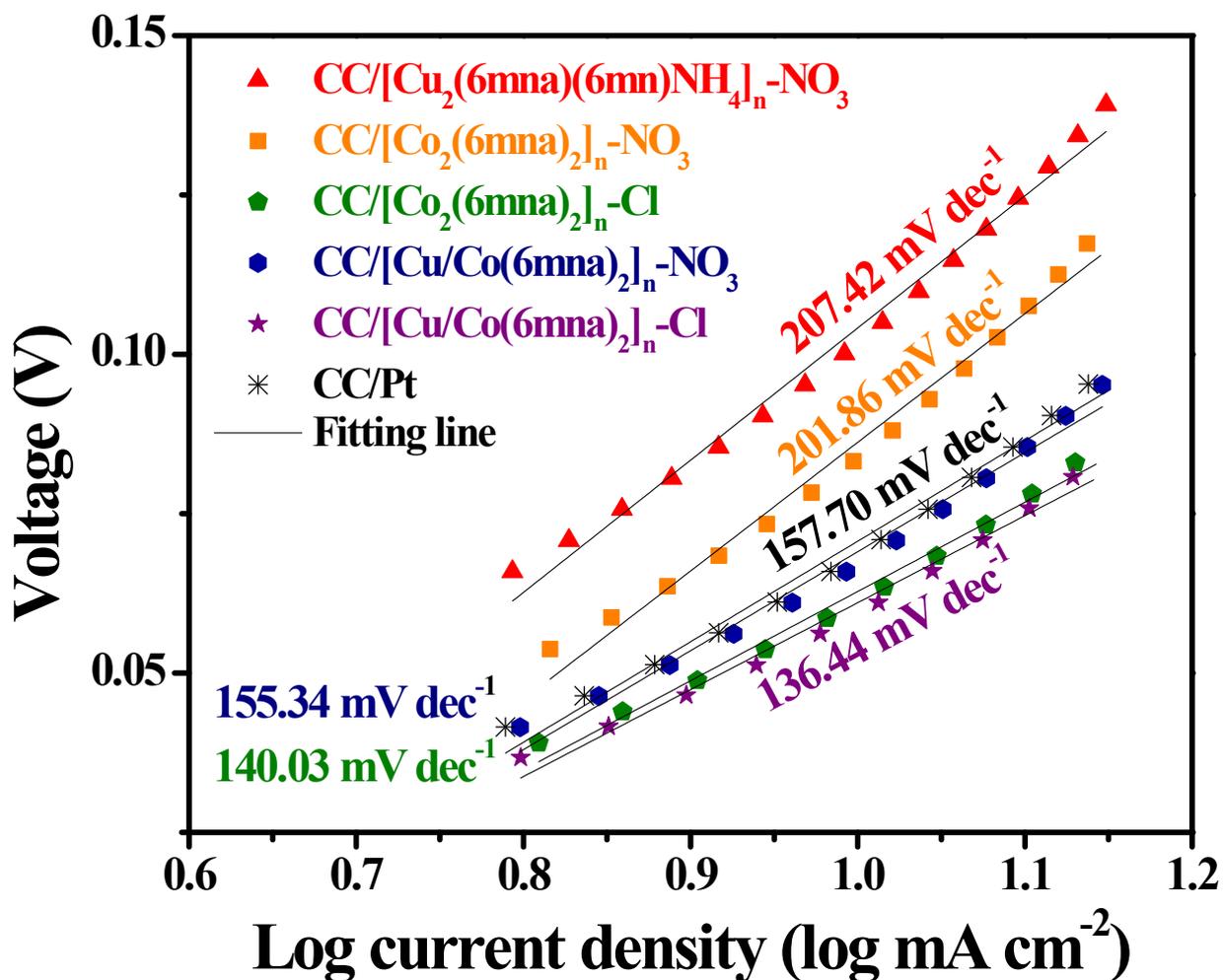
Fig. S17 Tafel polarization *V*–log *J* plots for various electrodes, measured in an iodide-based electrolyte.

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