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Supporting Information

Hierarchical urchin-like structure CoSe₂/CoSeO₃ electro-

catalysts for dye-sensitized solar cells: up to 19% at dim light

illumination

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1. Materials

Sodium selenite (Na₂SeO₃, 98%), ethanol (EtOH, 99.5%), isopropyl alcohol (IPA, 99.5%), titanium(IV) tetraisoproproxide (TTIP, >98%), lithium perchlorate (LiClO₄, \geq 98.0%), cetylmethylammonium bromide (CTAB, 99%), and 2-methoxyethanol were received from Sigma Aldrich. Lithium iodide (LiI, synthetical grade), iodine (I2, synthetical grade), and poly(ethylene glycol) (PEG, MW~20,000) were obtained from Merck. Cis-diisothiocyanato bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium (II) bis(tetrabutylammonium) (N719 dye), transparent TiO₂ paste (TL paste, Ti-nanoxide HT/SP, average diameter ~20 nm), and Surlyn® (SX1170-60, 60 μ m) were acquired from Solaronix (S.A., Aubonne, Switzerland). 1,2-Dimethyl-3-propylimidazolium iodide (DMPII) was brought from Tokyo Chemical Industry Co. Ltd. Cobalt(II) nitrate hexahydrate (Co(NO₃)₂·6H₂O, \geq 99.5%), triethanolamine (TEA, 99%), acetonitrile (ACN, 99.99%), and nitric acid (HNO₃, ca. 65% solution in water) were purchased from J. T. Baker. Acetone (99%), 4-tertbutylpyridine (tBP, 96%), guanidinium thiocyanate (GuSCN, \geq 99%), and tert-butyl alcohol (tBA, 96%) were obtained from Acros. 3-Methoxypropionitrile (MPN, 99%) was bought from Alfa Aesar. Commercial light-scattering TiO₂ particles (ST-41) with an average particle size of 200 nm were acquired from Ishihara Sangyo, Ltd.

2. Cell assembly

The photoanode consisted of a compact layer, a transparent layer, and a scattering layer, all of TiO₂. A precursor solution consisted of TTIP and 2-methoxyethanol (weight ratio: 1:3) was used to obtain the TiO_x compact layer (100 nm thickness) on an FTO substrate via spin-coating method. A transparent layer (~10 µm) was further coated on the compact layer by a doctor blade technique using a commercial transparent TiO₂ paste (TL paste, Ti–nanoxide HT/SP, average diameter ~20 nm). A scattering layer (~4 µm) was coated on the transparent layer by the same doctor blade technique using a home-made scattering paste, whose preparation will be described in detail at the next paragraph. Each TiO₂ layer was sintered at 500 °C for 30 min in an ambient environment before the next coating. The final sintered TiO₂ film (with an active area of 0.20 cm²) was immersed for 24 h at room temperature in a 5×10⁻⁴ M N719 dye solution containing a mixed solvent of ACN and tBA with the volume ratio of 1:1. The DSSC was composed of the N719-adsorbed TiO₂ photoanode, the CE and the electrolyte. The gap between the two electrodes was fixed by a 60 µm-thick Surlyn[®] (sealed by heating). The electrolyte, containing 1.2 M DMPII, 0.035 M I₂, 0.1 M GuSCN, and 0.5 M tBP in acetonitrile and 3-methoxypropionitrile (volume ratio = 1/1), was injected into the gap between these two electrodes by capillarity.

The above-mentioned scattering paste was made at home by a four-step procedure, as follows: (1) 0.5 M TTIP was added into 0.1 M nitric acid aqueous solution with constant stirring; this solution was heated to 88 °C and maintained at this temperature for 8 h; (2) the solution was cooled down to room temperature, transferred to an autoclave (PARR 4540, USA), gently heated to 240 °C, and kept at this temperature for 12 h (at this stage, the TiO₂ nanoparticles attain an average diameter of 20 nm); (3) the autoclaved TiO₂ colloid was concentrated to contain 8 wt% of TiO₂ nanoparticles; (4) the

scattering layer paste (SL paste) was obtained by the addition of 25 wt% of PEG and 100 wt% of ST-41 (with respect to the weight of TiO_2) to the concentrated- TiO_2 colloid.

3. Analytical techniques

Surface morphologies of various CEs were observed by a field-emission scanning electron microscope (FE-SEM, Nova NanoSEM 230, FEI, Oregon, USA), coupled with an energy dispersive X-ray spectroscope (EDX, model 7021-H, Horiba). Photovoltaic parameters and incident photon-toelectron conversion efficiency (IPCE) spectra of the DSSCs with various CEs were recorded by a potentiostat/galvanostat (PGSTAT 30, Autolab Eco-Chemie, Utrecht, the Netherlands). The power conversion efficiency of a DSSC was obtained under a light illumination of 100 mW cm⁻², using a class A quality solar simulator (XES-301S, AM1.5G, San-Ei Electric Co. Ltd., Osaka, Japan). The incident light intensity was calibrated with a standard Si cell (PECSI01, Peccell Technologies, Inc., Kanagawa, Japan). The IPCE curves of the DSSCs were obtained in the wavelength region of 400 to 800 nm by another class A quality solar simulator (PEC-L11, AM1.5G, Peccell Technologies, Inc., Kanagawa, Japan), equipped with a monochromator (model 74100, Oriel Instrument, California, USA). The incident radiation flux (φ) was measured via an optical detector (model 818-SL, Newport, California, USA) and a power meter (model 1916-R, Newport, California, USA). The ambient light measurements were performed under the T5 fluorescent lamp (TOA lighting, FH14D-EX, 14W, 6500K) and a height-tunable platform. The light lux and power density were measured by a sun spectroradiometer (S-2440 model II, Soma Optics Ltd., Tokyo, Japan).

Electro-catalytic properties of a film were quantified by cyclic voltammetry (CV) analyses. Cyclic voltammetry was performed in a three-electrode electrochemical system at a scan rate of 100 mV s⁻¹ with an electrolyte containing 10 mM LiI, 1.0 mM I₂, 0.1 M LiClO₄ and ACN solvent by using the above-mentioned potentiostat/galvanostat. The electrodes with Pt, $CoSe_2/CoSeO_3$ -NP, and $CoSe_2/CoSeO_3$ -UL were used as the working electrodes, and a Pt foil and an Ag/Ag⁺ electrode were used as the counter and reference electrodes, respectively. Electrochemical properties of the CEs were also quantified by Tafel polarization curves (Tafel curves) and electrochemical impedance spectroscopy (EIS); a symmetric cell, consisting of the same catalytic film on both anode and cathode, was used for these purposes. The data were recorded by the above-mentioned potentiostat/galvanostat equipped with an FRA2 module. The electrolyte consisted of 0.1 M LiI, 0.6 M DMPII, 0.05 M I₂, and 0.5 M tBP in MPN/ACN (volume ratio of 1/1) was used for Tafel analysis (scan rate of 50 mV s⁻¹) and EIS measurement. Under the open-circuit condition, the EIS analysis was performed between 10 mHz and 65 kHz with an AC amplitude of ±10 mV.

CE	η (%)	$V_{\rm OC}({\rm V})$	$J_{\rm SC}~({\rm mA~cm}^{-2})$	FF
CoSe ₂ /CoSeO ₃ -UL-0.6	7.40 ± 0.12	0.82 ± 0.00	14.04 ± 0.24	0.64 ± 0.00
CoSe ₂ /CoSeO ₃ -UL-1.0	7.82 ± 0.10	0.82 ± 0.08	14.20 ± 0.12	0.67 ± 0.00
CoSe ₂ /CoSeO ₃ -UL-1.4	9.29 ± 0.24	0.82 ± 0.01	16.09 ± 0.25	0.70 ± 0.00
CoSe ₂ /CoSeO ₃ -UL-1.8	9.08 ± 0.25	0.82 ± 0.09	14.95 ± 0.20	0.74 ± 0.00

Table S1. Photovoltaic parameters of the DSSCs with various CEs, measured at 100 mW cm² (AM 1.5G). The standard deviation data for each kind of DSSC were obtained using three cells.

Table S2. Photovoltaic parameters of the DSSC with the CEs of Pt obtained at 7000 lux (2.21 mW cm⁻²), 6000 lux (1.89 mW cm⁻²), and 4800 lux (1.55 mW cm⁻²). The standard deviation data were obtained from three devices for each condition.

Light irradiance (lux)	η (%)	$V_{\rm OC}$ (V)	$J_{\rm SC} ({\rm mA \ cm}^{-2})$	FF
7000	19.20 ± 0.20	0.66 ± 0.00	0.96 ± 0.00	0.70 ± 0.00
6000	18.12 ± 0.08	0.62 ± 0.00	0.75 ± 0.00	0.74 ± 0.00
4800	17.56 ± 0.09	0.61 ± 0.00	0.62 ± 0.01	0.71 ± 0.01



Figure S1. A ternary phase diagram: CTAB + toluene + aqueous solution of the precursor at 25 °C.



Figure S2. Photocurrent density-voltage curves of the DSSCs with various CEs, measured at 100 mW cm² (AM 1.5G).



Figure S3. The normalized stability data for the CoSe₂/CoSeO₃-UL CE up to 1,000 CV cycles.



Figure S4. Linear fitting of the capacitive currents at the reduction potential of the catalysts *vs.* the scan rate.



Figure S5. The spectrum of the T5 lamp at the light irradiances of 7000 lux (2.21 mW cm⁻²), 6000 lux (1.89 mW cm⁻²), and 4800 lux (1.55 mW cm⁻²).



Figure S6. Photocurrent density-voltage curves of the DSSC with the counter electrode of Pt, obtained at the light irradiances of 7000 lux (2.21 mW cm⁻²), 6000 lux (1.89 mW cm⁻²), and 4800 lux 1.55 mW cm⁻²).