Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2019

# **Supporting Information**

## Hierarchical urchin-like structure CoSe<sub>2</sub>/CoSeO<sub>3</sub> electro-

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

### illumination

Yi-June Huang,<sup>a</sup> Han-Ting, Chen,<sup>a</sup> Shiuan-Bai Ann,<sup>a</sup> Chun-Ting Li,<sup>b</sup> Jiann T. Lin,<sup>b</sup>

Chuan-Pei Lee, c,\* and Kuo-Chuan Ho<sup>a,d,e,\*\*</sup>

<sup>a</sup> Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan
<sup>b</sup> Institute of Chemistry, Academia Sinica, Nankang District, Taipei 11529, Taiwan
<sup>c</sup> Department of Applied Physics and Chemistry, University of Taipei, Taipei 10048, Taiwan
<sup>d</sup> Institute of Polymer Science and Engineering, National Taiwan University, Taipei 10617, Taiwan
<sup>e</sup> Advanced Research Center for Green Materials Science and Technology, National Taiwan University, Taipei 10617, Taiwan

#### 1. Materials

Sodium selenite (Na<sub>2</sub>SeO<sub>3</sub>, 98%), ethanol (EtOH, 99.5%), isopropyl alcohol (IPA, 99.5%), titanium(IV) tetraisoproproxide (TTIP, >98%), lithium perchlorate (LiClO<sub>4</sub>,  $\geq$ 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 TiO<sub>2</sub> paste (TL paste, Ti-nanoxide HT/SP, average diameter ~20 nm), and Surlyn® (SX1170-60, 60  $\mu$ 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(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O,  $\geq$ 99.5%), triethanolamine (TEA, 99%), acetonitrile (ACN, 99.99%), and nitric acid (HNO<sub>3</sub>, 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 TiO<sub>2</sub> 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 TiO<sub>2</sub>. A precursor solution consisted of TTIP and 2-methoxyethanol (weight ratio: 1:3) was used to obtain the TiO<sub>x</sub> 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 TiO<sub>2</sub> 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 TiO<sub>2</sub> layer was sintered at 500 °C for 30 min in an ambient environment before the next coating. The final sintered TiO<sub>2</sub> film (with an active area of 0.20 cm<sup>2</sup>) was immersed for 24 h at room temperature in a 5×10<sup>-4</sup> 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 TiO<sub>2</sub> photoanode, the CE and the electrolyte. The gap between the two electrodes was fixed by a 60 µm-thick Surlyn<sup>®</sup> (sealed by heating). The electrolyte, containing 1.2 M DMPII, 0.035 M I<sub>2</sub>, 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 TiO<sub>2</sub> nanoparticles attain an average diameter of 20 nm); (3) the autoclaved TiO<sub>2</sub> colloid was concentrated to contain 8 wt% of TiO<sub>2</sub> 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<sup>-2</sup>, 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 ( $\varphi$ ) 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<sup>-1</sup> with an electrolyte containing 10 mM LiI, 1.0 mM I<sub>2</sub>, 0.1 M LiClO<sub>4</sub> 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<sup>+</sup> 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 I<sub>2</sub>, and 0.5 M tBP in MPN/ACN (volume ratio of 1/1) was used for Tafel analysis (scan rate of 50 mV s<sup>-1</sup>) 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 <sub>2</sub> /CoSeO <sub>3</sub> -UL-0.6	$7.40 \pm 0.12$	$0.82 \pm 0.00$	$14.04\pm0.24$	$0.64 \pm 0.00$
CoSe <sub>2</sub> /CoSeO <sub>3</sub> -UL-1.0	$7.82 \pm 0.10$	$0.82 \pm 0.08$	$14.20\pm0.12$	$0.67 \pm 0.00$
CoSe <sub>2</sub> /CoSeO <sub>3</sub> -UL-1.4	$9.29 \pm 0.24$	$0.82 \pm 0.01$	$16.09 \pm 0.25$	$0.70 \pm 0.00$
CoSe <sub>2</sub> /CoSeO <sub>3</sub> -UL-1.8	$9.08 \pm 0.25$	$0.82 \pm 0.09$	$14.95 \pm 0.20$	$0.74 \pm 0.00$

**Table S1.** Photovoltaic parameters of the DSSCs with various CEs, measured at 100 mW cm<sup>2</sup> (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<sup>-2</sup>), 6000 lux (1.89 mW cm<sup>-2</sup>), and 4800 lux (1.55 mW cm<sup>-2</sup>). 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	$19.20 \pm 0.20$	$0.66 \pm 0.00$	$0.96 \pm 0.00$	$0.70 \pm 0.00$
6000	$18.12\pm0.08$	$0.62 \pm 0.00$	$0.75 \pm 0.00$	$0.74\pm0.00$
4800	$17.56 \pm 0.09$	$0.61 \pm 0.00$	$0.62 \pm 0.01$	$0.71 \pm 0.01$



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 cm<sup>2</sup> (AM 1.5G).



Figure S3. The normalized stability data for the CoSe<sub>2</sub>/CoSeO<sub>3</sub>-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<sup>-2</sup>), 6000 lux (1.89 mW cm<sup>-2</sup>), and 4800 lux (1.55 mW cm<sup>-2</sup>).



**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<sup>-2</sup>), 6000 lux (1.89 mW cm<sup>-2</sup>), and 4800 lux 1.55 mW cm<sup>-2</sup>).