Electronic Supplementary Information for

High performance of zinc stannate photoanode in dye sensitized solar cell with cobalt complex mediators

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1. Experimental Section

1.1 Chemicals and materials

All the chemicals, including tin(IV) chloride pentahydrate ($SnCl_4$, 98%, Sigma-Aldrich), zinc chloride ($ZnCl_2$, 98%, Sigma-Aldrich), *tert*-butylamine (TBA, 40 wt% aqueous solution, Acros), 4-*tert*-butylpyridine (4-TBP, Alpha), terpineol (Sigma-Aldrich) and ethyl cellulose (EC, 5~15 and 30~50 mPas, Sigma-Aldrich) were used as received without further purification. A 18 nm TiO_2 particle paste (18NR-T) were purchased from Dyesol. Sensitizer X73 ((E)-3-(6-(4-((6,9-bis(4-(hexyloxy)phenyl)-9H-carbazol-2-yl)(4-(hexyloxy)phenyl)amino)phenyl)-4,4-dihexyl-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl)-2-cyanoacrylic acid) were synthesized according to the reported methods.[1]

1.2 Synthesis of ZSO nanoparticles

In a typical synthesis, 0.82 g of $ZnCl_2$ and 0.65 g of $SnCl_4$ were dissolved into 38.53 g of deionized (DI) water. A 30 g of diluted TBA solution (25 wt%) was poured into the Zn/Sn mixture. After vigorous stirring for 5 min, the Zn_2SnO_4 (ZSO) precursor suspension with Zn/Sn/TBA (mole ratio) of 2:1:9 was transferred into a 100 mL autoclave. During the hydrothermal reaction, the suspension was heated to 200 ℃ for 12 h. After cooling to room temperature, ZSO precipitates were centrifuged with DI water for three times to remove the residual TBA absolutely.

1.3 Preparation of ZSO paste

ZSO paste was fabricated according to the reported method for preparing TiO_2 paste.[2] Briefly, ZSO precipitates were transferred into anhydrous ethanol solution after the removal of TBA. After 15 min dispersion with a 500 W ultrasonic probe, ZSO nanoparticles were centrifuged from the solution. Such procedure was repeated for three times in order to replace the water in the ZSO slurry with anhydrous ethanol. After that, 100 g of ethanol solution containing 8 wt% of ZSO nanoparticles were mixed with 32 g of terpineol, 2.24 g of EC (5~15 mPas) and 1.76 g of EC (30~50 mPas). The resultant suspension was agitated vigorously until a homogeneous colloid solution was obtained. Ethanol and residual water were subsequently removed with a rotary-evaporator. The ZSO paste was further grinded with a M-50 three-roll mill (EXAKT, Germany) for three times. The final paste for screening printing contains 16 wt% of ZSO, 8 wt% of EC and 64 wt% of terpineol.

1.4 Fabrication of photoelectrode and the assembly of device

ZSO photoanode was fabricated by using screen-printing technique. FTO-coated glass substrate (F-doped SnO_2, 15 Ω/square, Nippon Sheet Glass) was cleaned with de-ionized water, acetone and ethanol sequentially. The prepared ZSO paste was then coated onto the FTO sheet via screen-printing. After dried at 120 ^{o}C for 10 min, the deposited ZSO film was sintered at 500°C for 60 min, which gives rise to a semi-transparent ZSO photoanode.

Similar procedure was employed in the fabrication of TiO_2 photoanode. Before coating the TiO_2 colloid paste, a blocking layer was prepared by immersing FTO sheets into 40 mM aqueous $TiCl_4$ solution at 70°C for 30 min. TiO_2 colloid paste (18NR-T) was deposited onto the FTO substrates, which was followed by drying at 100 ^{o}C for 10 min, and sintered at 500°C for 30 min. The resultant TiO_2 film was placed into the $TiCl_4$ solution for the second time, and sintered at 500°C for another 30 min.

Dye sensitization was performed by immersing the ZSO or TiO_2 substrates into 300 μM *n*-butanol (BA)/ acetonitrile (ACN) (v/v=1:1) solution of an organic dye X73 for 24 and 12 h, respectively. The sensitized film was rinsed with anhydrous ethanol, and dried by air flow. Photoanode was assembled with a platinized counter electrode by using a 25 μm Surlyn hot-melt gasket (Solaronix, Switzerland) serving as spacer and sealant. Electrolyte based on cobalt complex was perfused into the assembly via vacuum backfilling. Platinized counter electrode was prepared by spin-coating 5 mM isopropanol solution of H_2PtCl_6 onto FTO substrates, and then heated to 395 °C for 15 min. The composition of cobalt complex based electrolyte is 0.25 M $[Co(II)(phen)_3]\ (PF_6)_2$, 0.05 M $[Co(III)\ (phen)_3](PF_6)_3$, 0.1M LiTFSI, and 0.5 M 4–tertpyridine (TBP) in acetonitrile.

1.5 Instruments and measurements

(1) Material analyses

The morphologies of ZSO and TiO_2 film were acquired with a MERLIN Compact field-emission scanning electron microscopy (Zeiss, Germany). A Talos F200X transmission electron microscopy (FEI, USA) was utilized for characterizing the morphologies of ZSO nanoparticles. Particle size distribution of ZSO aqueous dispersion was performed by Zetasizer Nano-ZS90 particle and molecular size analyzer (Malvern, UK). WAXS measurements were conducted by a D/max-2500 X-ray diffractometer (Rigaku, Japan) with Cu-K a radiation at a scanning speed of 1^{o}/min. Film thickness was determined by a DektakXT profilometer (Bruker, Germany). Specific surface area was determined by using ASAP 2020 nitrogen adsorption-desorption equipment (Micromeritics, USA) with the Brauner-Emmett-Tell (BET) approach. Diffuse reflection and specular transmittance spectra of the ZSO and TiO_2 films were measured by using a UV-2600 spectrophotometer (Shimadzu, Japan) with a 60 mm integrating sphere. Dye desorption was performed by immersing sensitized ZSO or TiO_2 films (5 mm diameter) into a mixture of dichloromethane and acetic acid (0.0072:1, v/v). The absorbance of the resultant solution measured by a UV-2600 spectrophotometer (Shimadzu, Japan) was employed for determining the dye loading of the sensitized films.

(2) Photoelectrochemical characterizations

Current-voltage (j–V) characteristics were determined with a computer controlled Keithley-2400 digital source meter (Keithley, USA). A solar simulator equipping with a 450 W xenon lamp and an AM 1.5 filter (Oriel 91160-1000, Newport, USA) was employed as the light source. The illumination intensity was adjusted to 1 sun (100 mW cm^{-2}) by using a NREL-calibrated Si solar cell. Incident power conversion efficiency (IPCE) spectra were measured by a home-made system. Light spectrum with the resolution of 10 nm was generated by combining a 300 W halogen lamp with a DK240 monochromator (Spectral Products, USA). Photocurrent was recorded by a Keithley-2400 digital source meter. Charge quantity was measured by charge extraction technique.[3] A LK2005A electrochemical system (Lanlike, China) was utilized for collecting the current signals as soon as the device was switched from open circuit to short circuit. Electrochemical impedance spectra (EIS) were collected by a Zennium electrochemical workstation (Zahner, Germany) in the dark. A serial of bias voltage was applied to the devices. Scanning frequency ranges from 100 kHz to 0.2 Hz, and modulation amplitude was set to 10 mV.

2. XRD peak list and the calculation of particle size

Table S1. The peak information from the XRD pattern.

No.	(h k l)	2θ /°	Inter-planar spacing/ Å
1	(1 1 1)	18.16	4.88
2	(2 0 0)	29.56	3.02
3	(3 1 1)	34.70	2.58
4	(2 2 2)	36.28	2.47
5	(4 0 0)	42.02	2.15
6	(3 3 1)	46.00	1.97
7	(4 4 2)	52.06	1.76
8	(5 1 1)	55.34	1.66
9	(4 4 0)	60.72	1.52
10	(5 3 1)	63.72	1.46
11	(5 3 3)	71.58	1.32
12	(6 2 2)	72.54	1.30

The particle size (*D*) is calculated by using the the Scherrer equation:

$$D = \frac{K\lambda}{\beta cos(\theta)} \qquad (S1)$$

where λ is the X-ray wavelength in nanometer (0.15405 nm), β is the peak width of the diffraction peak profile at half maximum height (FWHM) and K is a constant related to crystallite shape, taken as 0.89 herein. The (3 1 1) peak in the XRD pattern shows the 2θ of 34.70 ° and the FWHM of 0.25 °. By inserting these values into eqn S1, one obtains the particle size of 32.92 nm.

3. Enlarged SEM image of ZSO film

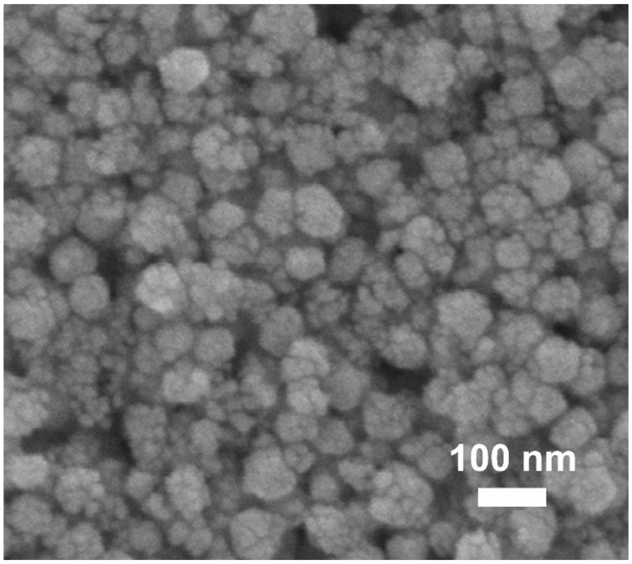

Fig. S1 Enlarged SEM image of the ZSO film with agglomerated nanoparticles.

4. Light harvesting efficiency spectra

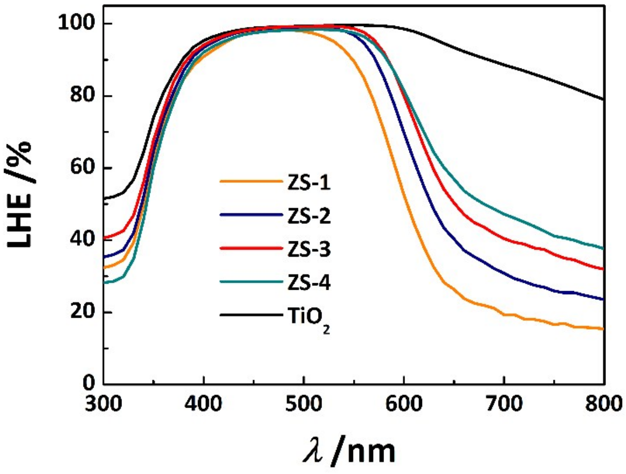

Fig. S2 Light harvesting efficiency (LHE) spectra of the cobalt complex based DSCs with ZSO and TiO_2 photoanodes.

5. Analyses on the impendence spectra

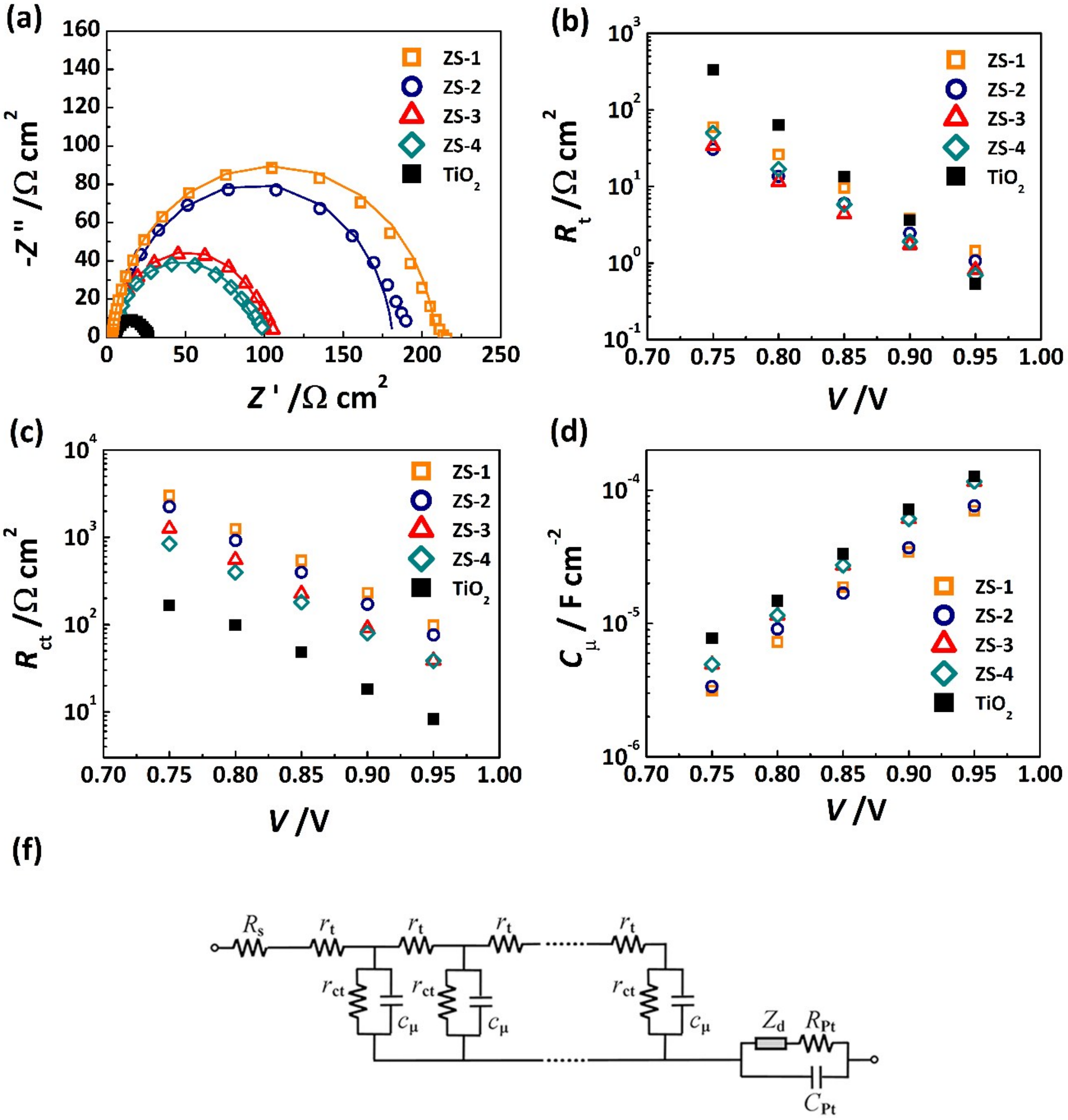

Fig. S3 Electrochemical impedance spectra of the DSCs based on ZSO and TiO_2. (a) Impedance curves at bias voltage of 0.9 V. Fitting results are indicated as the solid curves. Plots of electron transport resistance (b), charge transfer resistance (c) and dispersive chemical capacity (d) as a function of bias voltage. (f) The equivalent circuit for fitting the impedance spectra.[4] In the equivalent circuit, r_t is the transport resistance in the photoanode; r_{ct} and R_{Pt} are the charge transfer resistances at the nanocrystal/electrolyte interface and the counter electrode, respectively; c_μ and C_{Pt} are chemical capacitance at the nanocrystal/electrolyte interface and the counter electrode, respectively. Z_d is the Warburg element and R_s is the series resistance.

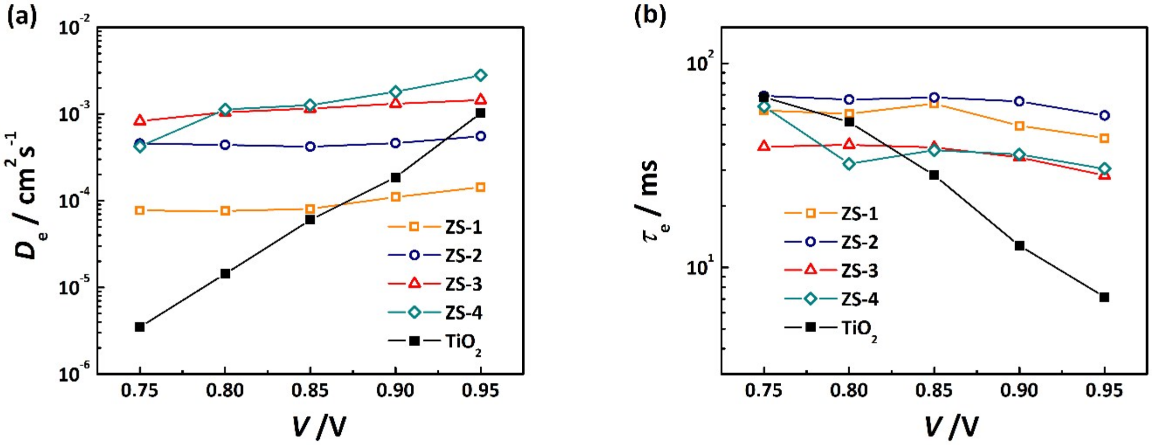

Fig. S4 Dependence of (a) effective diffusion coefficient and (b) electron lifetime on bias voltage. Here effective diffusion coefficient is evaluated according to the expression of $D_e = d^2/(R_t C_\mu)$. Electron lifetime (τ_e) is defined as the product of R_{ct} and C_μ.

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