# Supporting information

**Low Temperature-processed SnO$_2$-Cl for Efficient PbS quantum-dot solar cells via defect passivation**

Jahangeer Khan[a, +], Xiaokun Yang[a, c, +], Keke Qiao[a, +], Hui Deng[a], Jian Zhang[a], Zhiyong Liu[b], Waqar Ahmad[a], Jihong Zhang[d], Dengbing Li[a], Huan Liu [a], Haisheng Song[a*], Chun Cheng[c*], Jiang Tang[a]

[a]*Wuhan National Laboratory for Optoelectronics and School of Optical and Electronic Information, Huazhong University of Science and Technology, Luoyu Road 1037, Wuhan 430074, P. R. China*

[b]*State Key Laboratory of Digital Manufacturing Equipment and Technology, Huazhong University of Science and Technology, Wuhan 430074, P. R. China*

[c]*Department of Materials Science and Engineering and Shenzhen Key Laboratory of Nanoimprint Technology, South University of Science and Technology, Shenzhen 518055, P. R. China*

[d]*State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, Wuhan 430070, P. R. China*

[*]Corresponding author *E-mails:* songhs-wnlo@mail.hust.edu.cn (H. Song), chengc@sustc.edu.cn (C. Cheng)

[+]Those authors contribute equally to this work.

## Experimental section

### *Lead Sulfide Colloidal Quantum Dots (PbS CQDs) Synthesis*

The recipe has been modified from the literature.[1] For PbS CQDs synthesis, 0.9 gram yellowish lead oxide powder (PbO) was added to three-neck flask with 20 ml 1-octadecene (ODE) and 3 ml oleic acid. The system was pumped for at least 6 hours and the temperature was gradually increased to target temperature. After That, TMS (hexamethyldisilathiane) ODE solution was injected quickly into three-neck flask under the protection of $N_2$. The reaction took a few minutes and then it cooled to room temperature naturally. The PbS CQD product was washed with the help of acetone and centrifuged to collect PbS CQDs. This process was repeated 2-3 times to obtain clean PbS CQDs. Finally, PbS CQDs placed in vacuum box for 10-20 min to remove residual solvent. Finally, the as-obtained PbS QDs dissolved in hexane and octane (4:1) mixed solvents with a concentration of 30 mg/mL for ready use.

### *Preparation of ZnO film by sol-gel method*

The method was modified from the reported literature.[2] Typically, 1.5 gram zinc acetate dehydrate was added to 20 mL 2-methoxyethanol and 500 μl monoethanolamine was utilized as stabilizer. The solution was stirred at 60 °C for 8 hours to obtain a transparent precursor solution. For ZnO film preparation, ZnO precursor was spin-coated on a pre-cleaned FTO/glass substrate at 4000 rpm/min for 30 s, further annealed at 400 °C for 15 min. This process was repeated a few times to reach the required thickness.

### *Preparation for $SnO_2$-Cl ETL*

The $SnO_2$-Cl ETL was synthesized from modified literature.[3] $SnO_2$ precursor was prepared by dissolving $SnCl_2 \cdot 2H_2O$ in ethanol with varied concentrations. Accurate amount of $SnO_2$ precursor was dropped on cleaned FTO and span at 4000-5000 rpm/min for 40 s. Then the film was baked at 200 °C for 60 min. This process was repeated for 3-4 times to obtain the required thickness. Such baking temperature treated $SnO_2$ layer was denoted as $SnO_2$-Cl. Different baking temperature $SnO_2$ samples were also prepared for chlorine role investigation.

## Device fabrication

The obtained ZnO/FTO and SnO$_2$/FTO were utilized as the substrates. For FTO/SnO$_2$/PbS-EMII/PbS-EDT/Au devices, PbS QD solution was dropped on SnO$_2$/FTO substrate and span with 2500 rpm/min for 30 second. Then EMII-methanol solution was dropped on QD surface, kept for 1 min and span for 20 s. The EMII ligand exchanged film was washed three times by methanol to remove the non-reacted ligand residue. The above PbS-EMII QD deposition process was repeated for 8-10 times to reach the required absorber thickness. At the end of active layer, another two layers of PbS-EDT QDs were spin-coated and the ligand was changed into EDT. The as-obtained QD film was stored overnight. Eventually 80 nm Au was coated on PbS-EDT layer through thermal evaporator. For PbS-TBAI QDs layer deposition, the procedure is the same as PbS-EMII layer except that the ligand was changed into TBAI.

## Device Characterization

The current density-voltage (J-V) characteristics were measured using Keithley 2400 (J-V) digital source meter under simulated AM1.5G (100 mW/cm$^2$) illumination from a 450 W Xenon lamp (Oriel, Model 9119, Newport) as the light source in air at room temperature. The light intensity was calibrated with a standard Si solar cell (Oriel, Model 91150V, Newport). The device was covered with a metal mask with an aperture area of 0.04 cm$^2$ during efficiency measurement. The external quantum efficiency (EQE) measurements were taken by a home-made setup containing a Keithley 2400 Source Measure unit and Newport monochromator.

## Material characterization

The transmittance of ZnO or SnO$_2$-Cl film and absorbance of PbS CQDs were obtained using UV-vis spectrophotometer (PerkinElmer instrument, Lambda 950). The mobility of the SnO$_2$-Cl and ZnO films were measured by Hall Effect (Ecopia, HMS-5500, Korea). Hall effect measurement was conducted on a oxide film in dark. All four electrodes are gallium. A Keithley 2400 source meter was used to apply DC current and a Keithley 4200 source meter was used to record the Hall voltage. The majority carrier was determined to be electrons based on the Hall voltage sign. The free electron carrier concentration (n) in film was determined by

$n = -\dfrac{IB}{eV_H t}$, where I is the applied bias current, B is the magnetic field, $V_H$ is the measured

Hall voltage, t is the thickness of the film, and e is the elementary charge. The mobility is determined by μ=σ/ne. The trap densities of ZnO and $SnO_2$-Cl films were measured using space-charge-limited current (SCLC) model with an electron-only devices of FTO/Ag/metal oxide/Ag. The dark J-V curve was recorded using a B1500A semiconductor characterization system (Figure S2) and used to calculate the trap-state density by[4]

$$V_{TFL} = \frac{en_{trap}L^2}{2\varepsilon_0\varepsilon} \qquad (S1)$$

where L is the thickness of film, $\varepsilon_0$ is the vacuum permittivity, $\varepsilon$ is the relative dielectric constant for the $SnO_2$ ($\varepsilon_{SnO_2}$=10) or ZnO ($\varepsilon_{ZnO}$=17), which were obtained from *C-f* measurements[5] in Fig. S5. At low electric field, an Ohmic region is confirmed. The J–V characteristics change at $V_{TFL}$ where the current density exhibits a sharp rise, indicating the transition into the trap-filled limit, where all trap states are occupied by the injected charge carriers. Thus, we could obtain $V_{TFL}$ from current density sharp rise. Utilizing $V_{TFL}$ values, $n_{trap}$ values could be calculated from Equation S1.

X-ray photoelectron spectroscopy (XPS) and Ultraviolet photoelectron spectroscopy (UPS) measurement were carried out in a Kratos AXIS Ultra-DLD with an Al Kα radiation source. Scanning electron microscopy (SEM) images were obtained using FEI Nova Nano SEM 450. Photoluminescence (PL) measurements were carried out using home-made system with 800 nm laser (Ti-Sapphire laser) from Wuhan University of Technology.

**AC impedance spectroscopy measurements** were performed using an elecctrochemical station (Autolab PGSTAT302N, Metrohm Autolab, Netherlands) under simulated AM1.5G (100mW/cm$^2$) illumination with open-circuit conditions. The frequencies ranging from 0.1 kHz to 1 MHz with an alternating-signal amplitude of 10 mV. The relaxation process of carriers can be described as following[6]:

$$I(t) = Ae^{\frac{-t}{\tau_1}} \qquad \text{(S2)}$$

where A is a constant and $\tau_1$ is defined as the lifetime of the carriers, t is the variation of time. The relaxation process described by Eq. (S2) has a characteristic frequency, and it can be described by the following equation:[6]

$$w_1 = \frac{1}{\tau_1} \qquad \text{(S3)}$$

where the frequency $w_1$ can be extracted from EIS results.

**The capacitance–voltage (C – V)** measurements were acquired with an Agilent 4200A at a frequency of 10 kHz and AC signal of 50 mV, scanning from -1 to +1 V, with a step of 50 mV. The built-in potentials ($V_{bi}$) of the devices were obtained from a Mott–Schottky plot. The depleted width of QD layer ($W_D$) at zero bias according to the following equation:[5]

$$W_D = \frac{1}{N_A} \left[ \frac{2\varepsilon_{QD}\varepsilon_0}{q\left(\frac{1}{N_D} + \frac{1}{N_A}\right)} V_{bi} \right]^{\frac{1}{2}} \qquad \text{(S4)}$$

and

$$N_A = \frac{2}{A^2 q \varepsilon_{QD}\varepsilon_0 \frac{d}{dV}(\frac{1}{C^2})} \qquad \text{(S5)}$$

where $N_A$ and $\varepsilon_{QD}$ were the PbS CQD carrier density and dielectric constant respectively which were taken from previous work,[5] $\varepsilon_0$ is the vacuum permittivity, $N_D$ is the ZnO or SnO$_2$ carrier density from the Hall Effect results, and $V_{bi}$ is the built in potential of QDs devices.

**The transient photovoltage (TPV)** and **transient photocurrent decay** (TPC) measurements were carried out using home-made system. A white light bias on the samples was generated from an diode array (Lumiled) as constant light, a ring of red

light-emitting pulse diode (LED, Lumiled) controlled by a fast solid-state switch (the pulse widths were 1 ms). The transient photocurrent was measured using 20 ohm external series resistance to operate the device in short circuit. Similarly, transient photovoltage was applied using 1 M ohm external series resistance to operate the device in open circuit. The voltage output was recorded on an oscilloscope directly connected with the cells. The TPC and TPV results were fitted to a mono-exponential decay function in order to extract the transport and recombination times. The charge transport ($\tau_t$) and recombination time ($\tau_r$) were defined as the time when the photocurrent or photovoltage decayed to 1/e of the their initial values.

# Reference

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6    H. Wang, Y. Wang, B. He, W. Li, M. Sulaman, J. Xu, S. Yang, Y. Tang and B. Zou, *ACS Appl. Mater. Interfaces* 2016**, 8**, 18526-33.
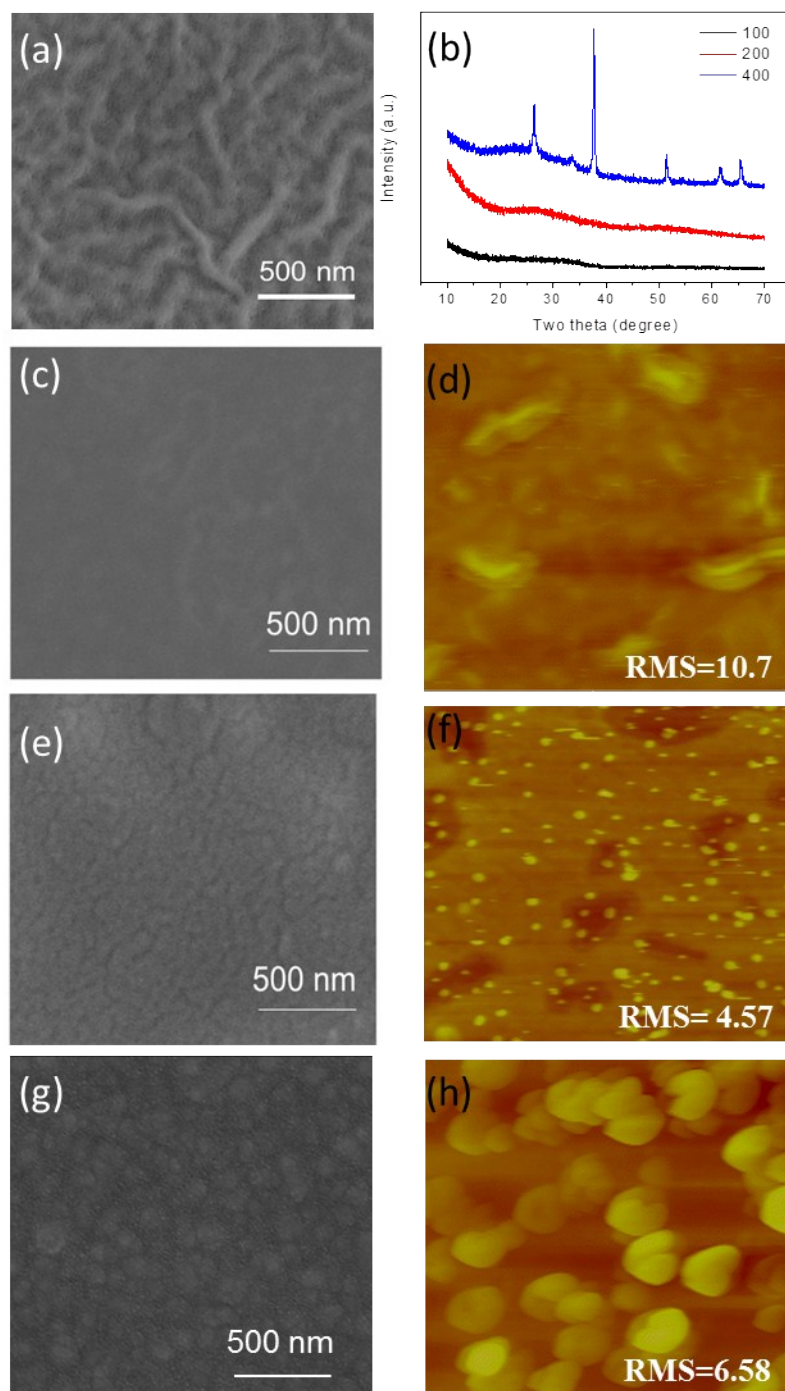
FigureS1. Window layer characterizations. (a) SEM images of ZnO film. (b) XRD spectra of $SnO_2$ film annealed by 100 °C, 200 °C and 400 °C treatment, respectively. (c, d) 100 °C annealed $SnO_2$ samples; (e, f) 200 °C treated $SnO_2$ samples; (g, h) 400 °C annealed $SnO_2$ samples.
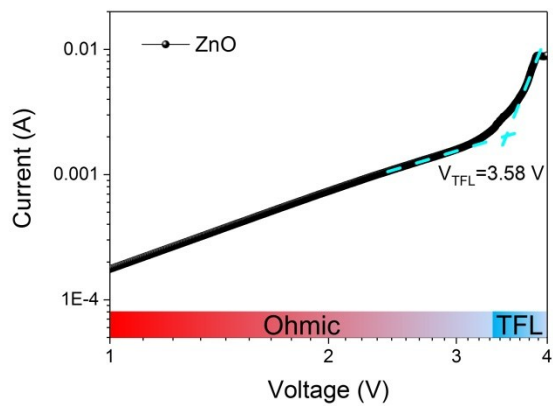
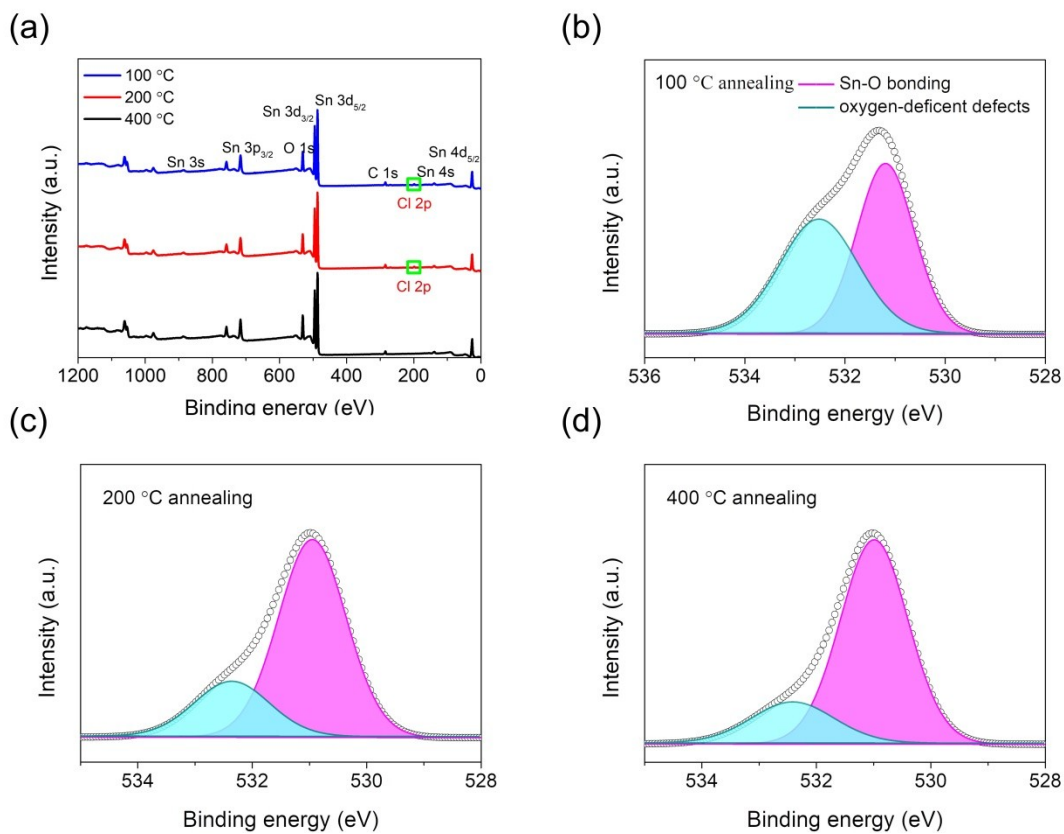**Figure S2.** Log ($J$)–log ($V$) plots for ZnO film by using SCLC technique.

**Figure S3.** (a) XPS full spectra and O 1s peaks of various $SnO_2$ films via (b) 100 ℃, (c) 200 ℃ and (d) 400 ℃ thermal annealing.

Table S1. The performances of PbS solar cells fabricated with different thermal annealing $SnO_2$ films as ETLs.

| Device | Voc (V) | Jsc (mA/cm²) | FF | PCE (%) | Rs (Ω·cm²) | Rsh (Ω·cm²) |
|--------|---------|--------------|------|---------|------------|-------------|
| 100 °C | 0.50 | 9.16 | 0.36 | 1.64 | 23.48 | 81.2 |
| 200 °C | 0.57 | 25.63 | 0.64 | 9.37 | 3.23 | 363.3 |
| 400 °C | 0.52 | 16.84 | 0.35 | 3.1 | 15.45 | 97.43 |
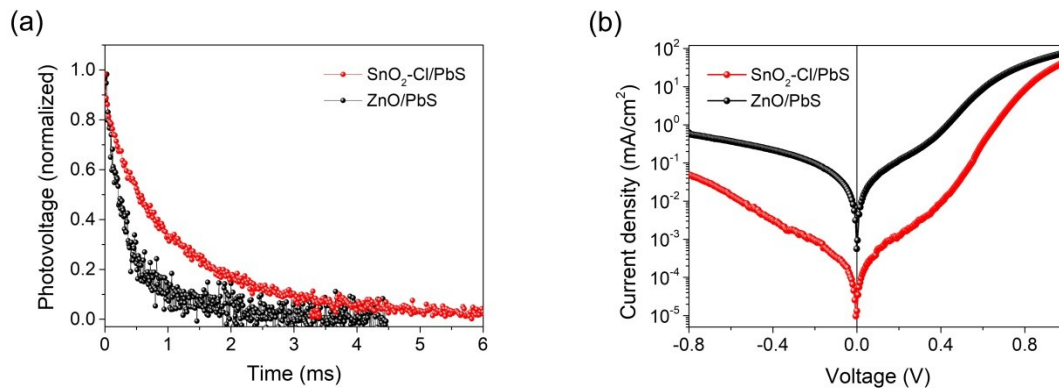
**Figure S4.** (a) Transient Photo voltage (TPV) of QDs solar cell with $SnO_2$ and ZnO layer. (b) Dark current of QDs solar cells with $SnO_2$ and ZnO as ETLs.
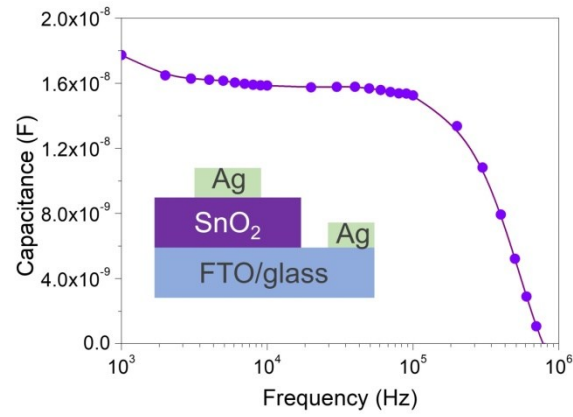
**Figure S5.** *C-f* measurement data of $SnO_2$ films with Ag/FTO/$SnO_2$/Ag structure from $10^3$ HZ to $10^6$ HZ. The ε of $SnO_2$ can be obtained from the following formula: $C = \dfrac{\varepsilon_r \varepsilon_0 S}{d}$, where S is active area and d is the thickness of $SnO_2$ layer. $\varepsilon_r$ is the relative dielectric constant of $SnO_2$, and $\varepsilon_0$ is the vacuum permittivity.
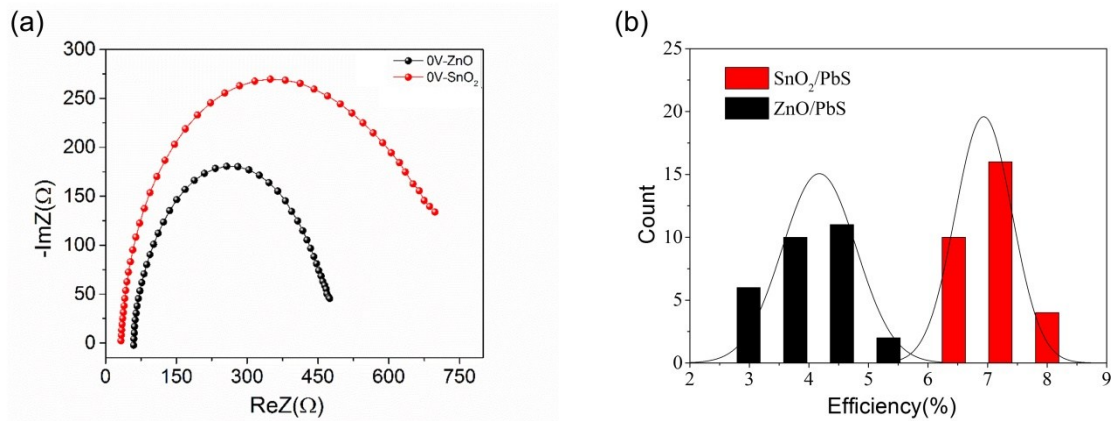
**Figure S6.** (a) Impedance spectra of $SnO_2$ and ZnO devices at 0V bias voltage and constant illumination condition. (b) Device performance distribution based on the device structure of $FTO/SnO_2$-Cl or ZnO/PbS-TBAI/PbS-EDT/Au.
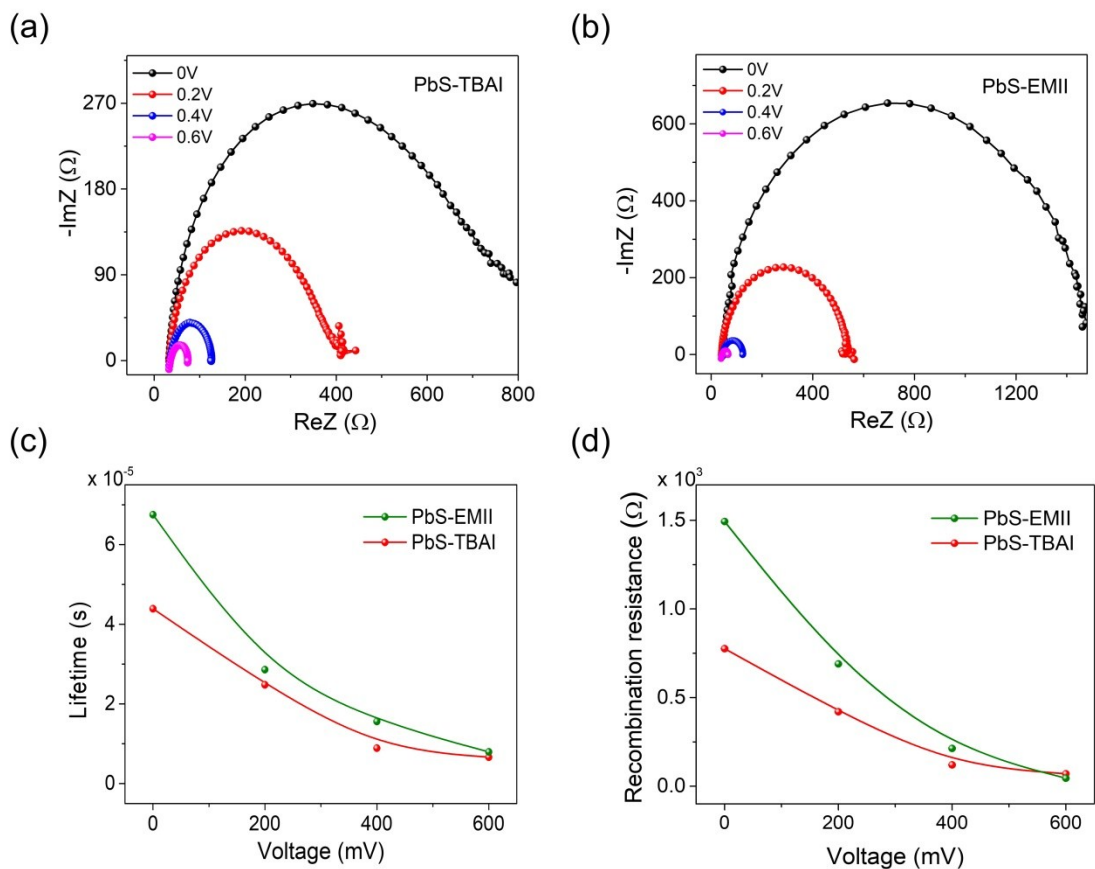
**Figure S7. (**a) Impedance spectra of PbS QD solar cell with TBAI treatment at various bias voltages and constant illumination. (b) Impedance spectra of PbS QD solar cell with EMII treatment at various bias voltages. (c) Life time of same $SnO_2$-Cl device with different ligands under illumination conditions. (d) Recombination resistance ($R_{rec}$) of QDs solar cells with different ligands (TBAI, EMII) under illumination conditions.
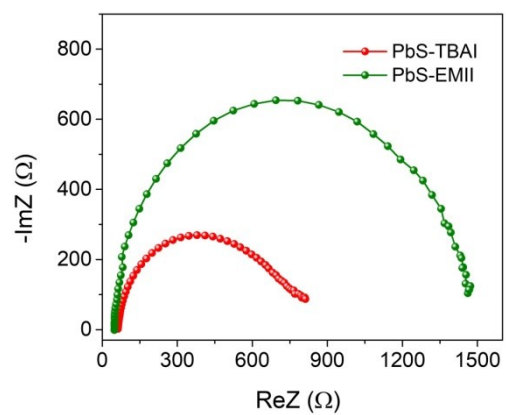
**Figure S8.** Impedance spectra for SnO$_2$-Cl based devices using TBAI and EMII ligands at 0V bias voltage under illumination.
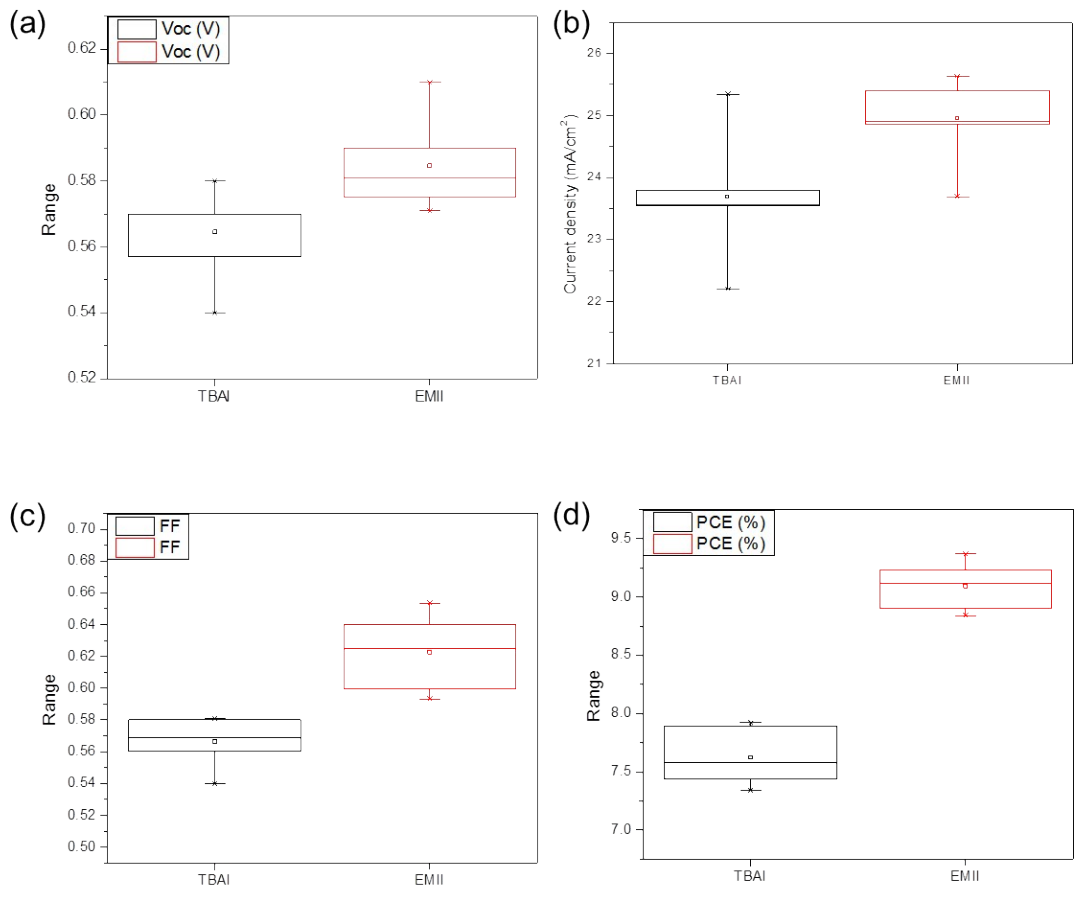
**Figure S9.** Statistical analysis for TBAI and EMII ligand based QD solar cells.