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Electronic Supplementary Information

Inverted Schottky PbS colloidal quantum dot solar cells with enhanced carrier extraction and air-stability

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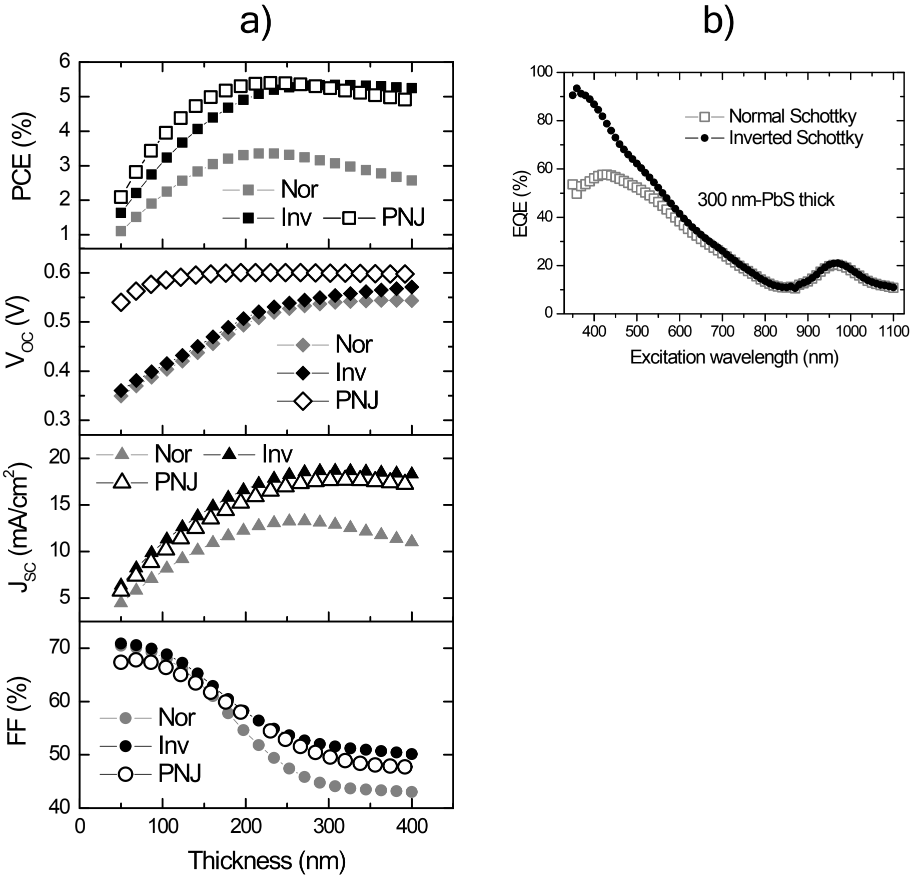

Figure S.1 SCAP simulation results for normal Schottky, (abbreviated as Nor), inverted Schottky (abbreviated as Inv), and *p-n* junction (abbreviated as PNJ), solar cells with varying the thickness of PbS QD film. a) from top to bottom: AM1.5 power conversion efficiency (*PCE*), open circuit voltage (V_{OC}), short circuit current density (J_{SC}), and fill factor (*FF*). b) calculated external quantum efficiency (*EQE*) for normal and inverted Schottky devices with a 300nm-thick PbS CQD layer. The PbS CQDs have the first excitonic peak at 970 nm.

The SCAP calculations were carried out as reported for CQD solar cells.[1,2] We used doping density of PbS QD film N_A = 5 x 10^{16} cm^{-3}, conduction band (E_C) and valence band (E_V) energy to be -3.8 eV and -5.1 eV (with respect to the vacuum level), respectively. Workfunction (*wf*) was assumed to be -3.9 eV for LiF/Al and -4.8 eV for ITO in the normal Schottky cell and -3.9 eV for low-*wf* TCO and -4.8 eV for high-*wf* metal in the inverted Schottky cell. To calculate the performance of *p-n* junction solar cell, TiO_2 is used as n-type semiconductor whose doping density (N_C), E_C, and E_V were assumed to be 10^{19} cm^{-3}, 4.1 eV (with respect to the vacuum level), and 7.3 eV (with respect to the vacuum level), respevtively.[2] The *PCE* of inverted Schottky cell is comparable to PNJ cell.

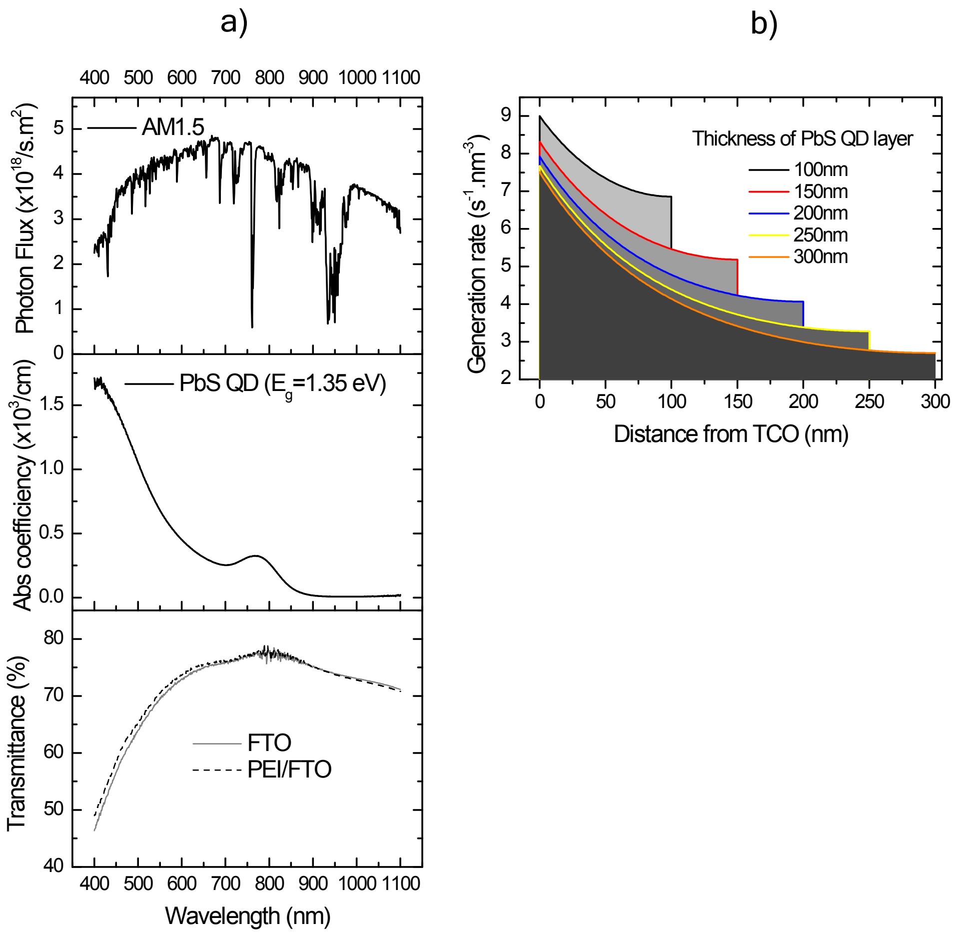

Figure S.2 (a) Photon flux (top), absorption coefficiency (middle) and transmittance of FTO and PEI-modified FTO, noted as low-work-function FTO in the main text, (bottom) data used to calculate the carrier generation rate. (b) The total carrier generation rate within PbS QD layer of different thickness (shown as legend) obtained by integrating equation (1) shown in the main text over 400-1100 nm range. It is apparent from (b) that the carrier generation rate at the front of CQD layer, near TCO, is always higher than elsewhere.

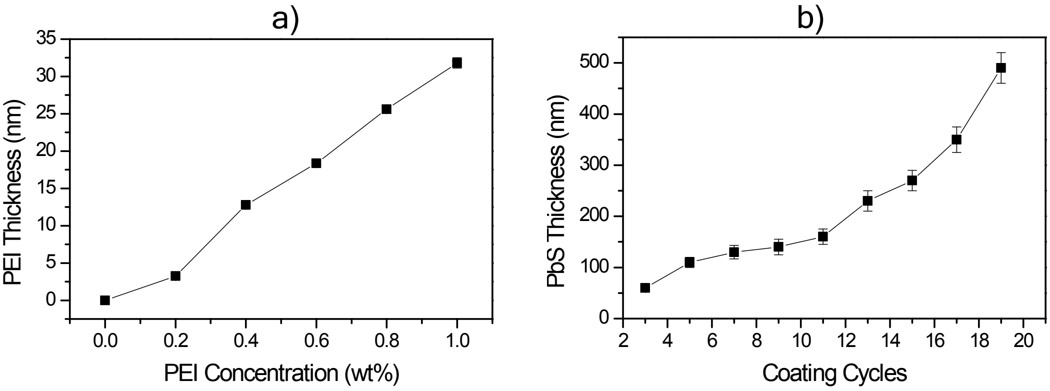

Figure S.3 a) Concentration-dependence of the thickness of the PEI layer. The coating conditions were: room temperature; coating speed at 5000 rpm with 5 second acceleration time; the films were annealed at 100°C in N_2-filled glove box for 10 minutes. The thickness was measured by mean of ellipsometry spectroscopy (SE). b) The dependence of PbS QD layer thickness on the number of coating cycle. The concentration of oleic acid capped PbS CQDs in octane is 30 mg/ml. 1,2-ethanedithiol 1 volume percent in acetonitrile was used to perform solid-state ligand exchange with the oleic acid. The coating was carried out while the substrate pinned at a speed of 2500 rpm.

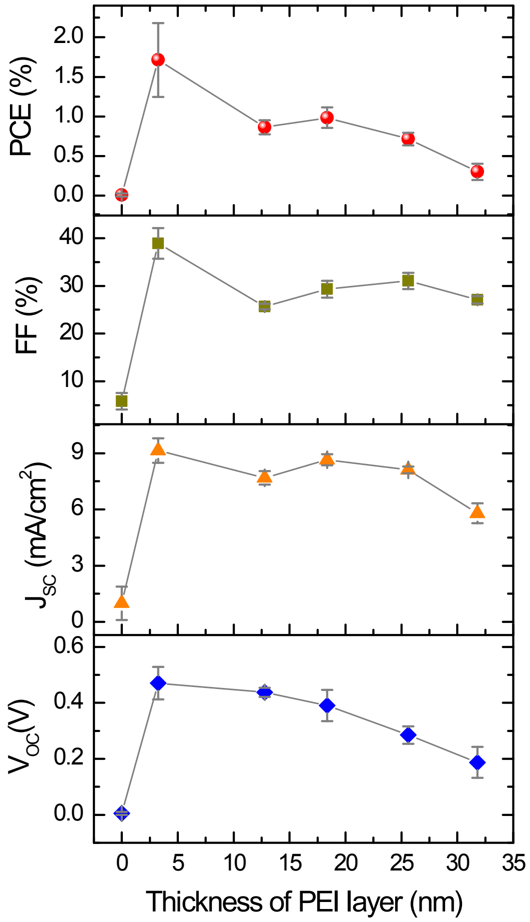

Figure S.4 Effects of PEI thickness on the performance of inverted Schottky solar cell. Cells have a common structure: Low-*wf* FTO/100 nm-thick PbS QD (E_g = 1.49 eV)/10 nm MoO_x/80nm Au-Ag. The optimal thickness of PEI is about 3 nm, which is obtained by using a 0.2 wt% solution of PEI in methoxymethanol, see Fig. S3(a).

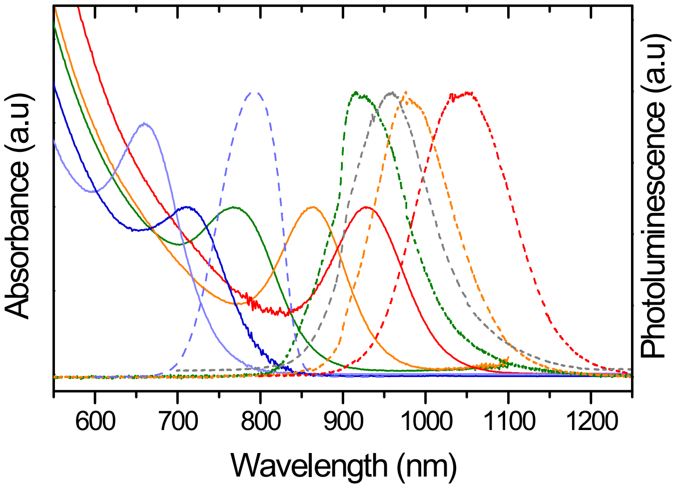

Figure S.5 UV-vis absorption (solid spectra) and photoluminescent (PL) (dotted spectra) of PbS CQDs dissolved in tetrachloroethylene (TCE) of different sizes in tetrachloroethylene. The absorbance was adjusted to clarify the first excitonic peak. The PL spectra were normalized. The energy bandgap (E_g) of CQDs were calculated from the PL peak.

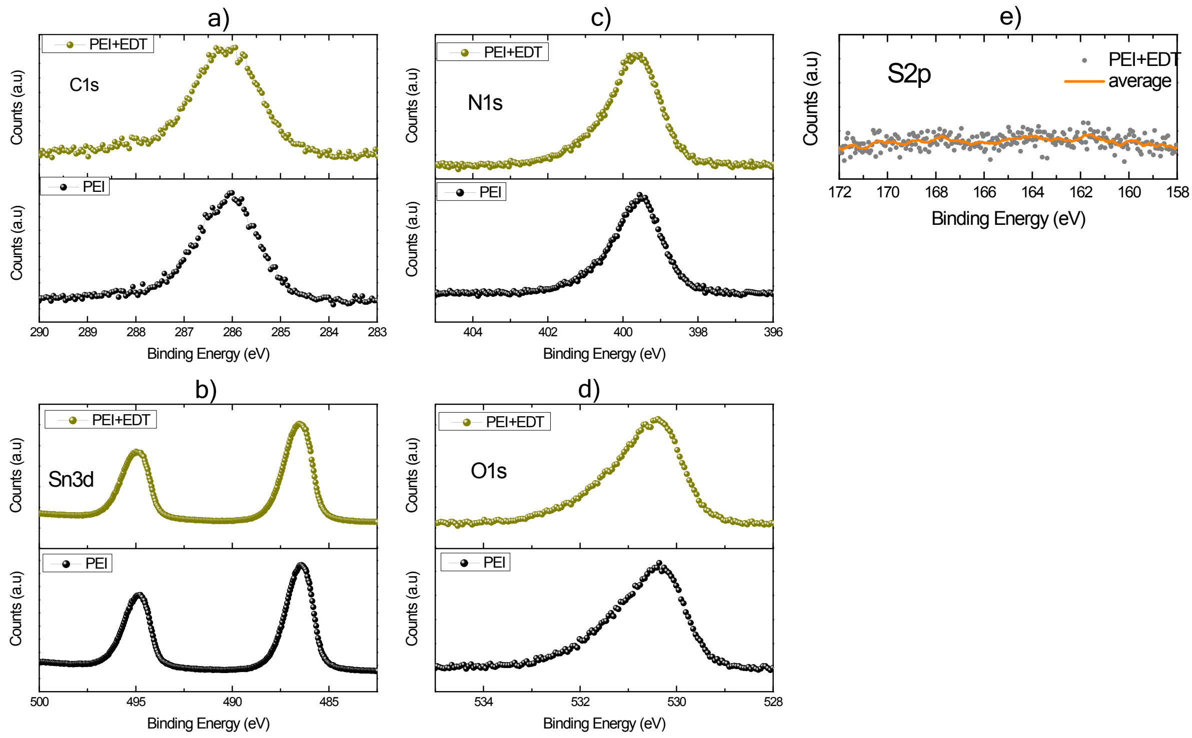

Figure S.6 XPS spectra of PEI or PEI treated with 1,2-ethanedithiol (EDT) thin layer on FTO substrate showing a) C1s, b) Sn3d, c) N1s, d) O1s, and e) S2p region, respectively. Most of N atoms in the PEI are in the neutral state whose binding energy is of 399 eV. The fact that the XPS spectrum of PEI is largely unchanged (from panel **a** to **d**) and that the S2p peak is lacking (panel e) indicates that the PEI layer maintains and does not react with PEI during the QD coating step.

In order to test whether the PEI layer is physicochemically affected by the QD coating step, X-ray photoelectron spectroscopy (XPS) analyses were conducted on two sample sets: PEI on FTO (PEI/FTO) and PEI+EDT/FTO that were obtained by treating the pre-formed PEI/FTO 5 cycles of with EDT solution (1 vol% in acetonitrile, 0.05 ml) - rinsing with acetonitrile (0.08 ml). EDT and acetonitrile were used as cross-link ligand and solvent in the QD coating process. XPS results indicate that the PEI layer is not chemically affected by EDT and that it maintains on FTO after the QD coating.

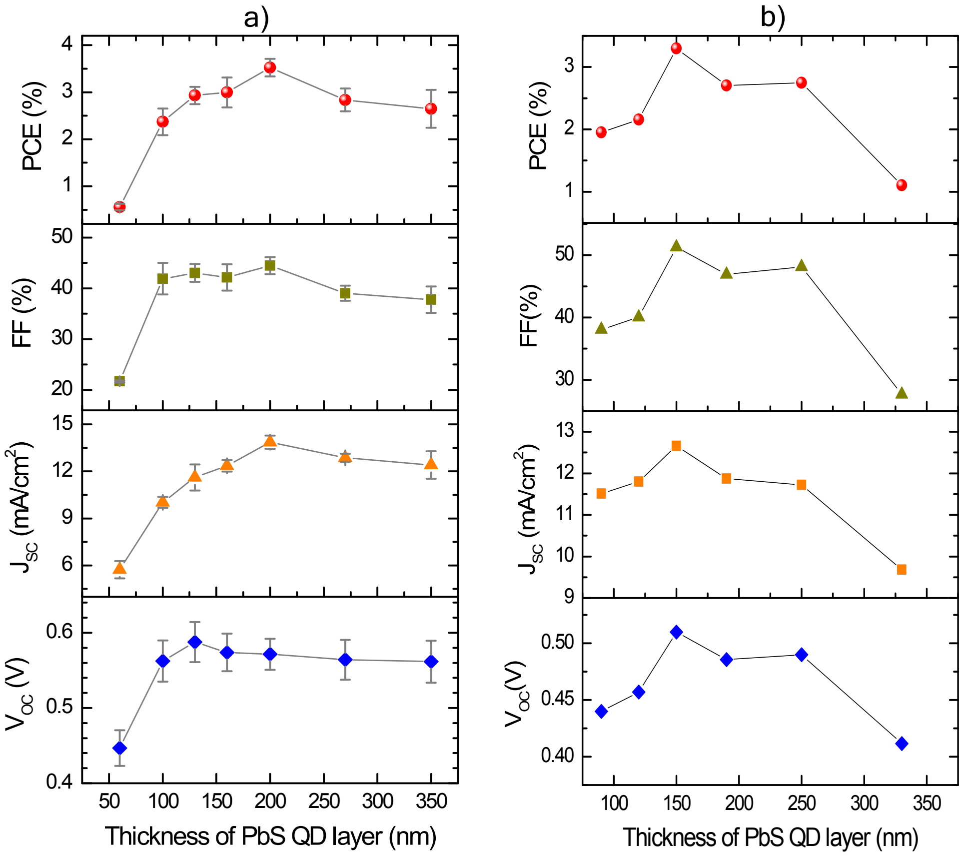

Figure S.7 Effects of PbS QD layer thickness on the performance of inverted (a) and normal (b) Schottky solar cell. The inverted cells have a common structure: Low-*wf* FTO/PbS CQD/10 nm MoO_x/80 nm Au-Ag. The bandgap of PbS CQDs is 1.49 eV. The normal Schottky cells have a common structure ITO/PbS QD/1 nm LiF/100 nm Al. The thickness of the PbS QD layer was varied by increasing the coating cycle as shown in Fig. S3(b).

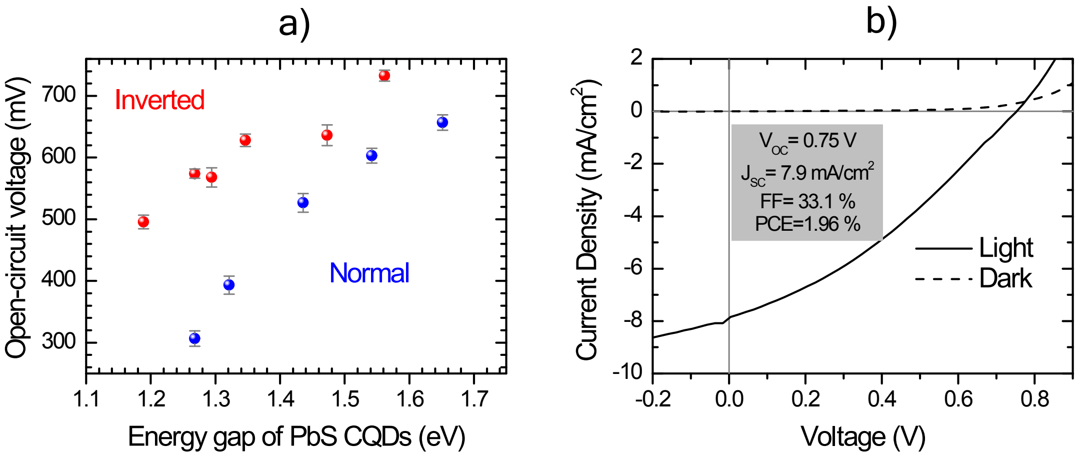

Figure S.8 a) Bandgap-dependence of V_{OC} of the inverted Schottky (red points) and normal (blue points) solar cells. The structure of the inverted cells is: Low-*wf* FTO/200±20 nm PbS QDs/10 nm MoO_x/80 nm Au-Ag. The structure of the normal cells is: ITO/100±10nm PbS QDs/1 nm LiF/100 nm Al. Each data point was the average of six devices on a single substrate. b) J-V characteristics of the device yielding the highest V_{OC} (0.75 V) under dark (dashed curve) and simulated AM1.5 illumination (solid curve) conditions. Insert in (b) is the cell performance under AM1.5.

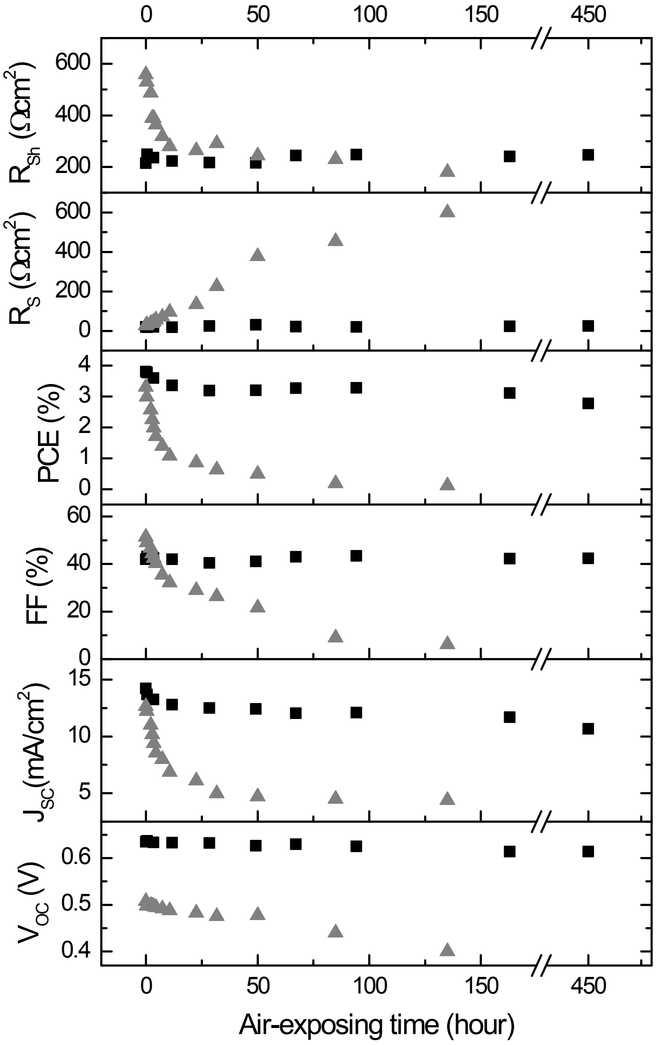

Figure S.9 The variations in shunt-resistance (R_{Sh}), series-resistance (R_S), Am1.5 power conversion efficiency (PCE), fill-factor (FF), short-circuit current density (J_{SC}), and open-circuit voltage (V_{OC}) of the champion inverted (black-square) and normal (gray-triangle) Schottky PbS CQD SCs after exposing to air with different period of times.

ESI. References

1. M. Burgelman, P. Nollet and S. Degrave, *Thin Solid Films*, 2000, **361**, 527.

2. D. Zhitomirsky, I. K. Kramer, A. J. Labelle, A. Fischer, R. Debnath, J. Pan, O. M. Bakr, and E. H. Sargent, *Nano. Lett.*, 2012, **12**, 1007.