

Enhanced photovoltaic performance and morphological control of PbS counter electrode grown on functionalized self-assembly nanocrystals for quantum-dot sensitized solar cells via cost-effective chemical bath deposition

Chebrolu Venkata Thulasi-Varma, S. Srinivasa Rao, I Kanaka Durga, Soo-Kyoung Kim, Tae-Su Kang, Hee-Je Kim*

School of Electrical Engineering, Pusan National University, Gumjeong-Ku, Jangjeong-Dong, Busan 609-735, South Korea

*Corresponding author. Tel.: +82 51 510 2364; fax: +82 51 513 0212.

E-mail address: heeje@pusan.ac.kr (H.-J. Kim).

†Electronic supplementary information (ESI) available: Dark current Vs potential curves of QDSSCs with different counter electrodes under dark condition, Additional characterization data from CV analysis of PbS and Pt CEs, Parameters of the quantum dot-sensitized solar cell using with different thickness as counter electrodes measured under AM 1.5 illumination, PbS CE sheet resistance Vs thickness are shown in Fig S1, S2, S3, and S4.

Dark current-Voltage characteristics of QDSSCs with PbS and Pt CEs:

The dark current-voltage characteristics of QDSSCs with PbS and Pt CEs are shown in fig. S1. It provides further insight into the changes occurring during the time periods of deposition process. In the dark under forward bias, electrons enter into the TiO₂ cell and react with S_X^{2-} , which means reduce the S^{2-} ions and the resultant S^{2-} is oxidized to S_X^{2-} at the counter electrode. This information can be used to estimate the charge recombination at the

interface between the CE and polysulfide electrolyte.¹ As seen in the figure, the dark current onset potential of Pt CE gradual increase when compared to PbS CEs. This can be attributed to the decrease in the catalytic activity of the sulfur poisoned Pt CE. The oxidation reaction of Pt CE shows limited on the FTO/TiO₂ interface, which may successively turn leads to the concentration depletion of S_x^{2-} ions and increases the dark current potential. A similar trend was observed in DSSCs with a I^- / I_3^- redox electrolyte upon varying R_{CT} at the counter electrode interface.² on the other hand, the PbS thin films presents low dark current when compared to Pt electrode, which means the deposition time periods of PbS CEs, confirms the good adherence to the FTO substrate, and robust, and greater catalytic features in the QDSSCs.

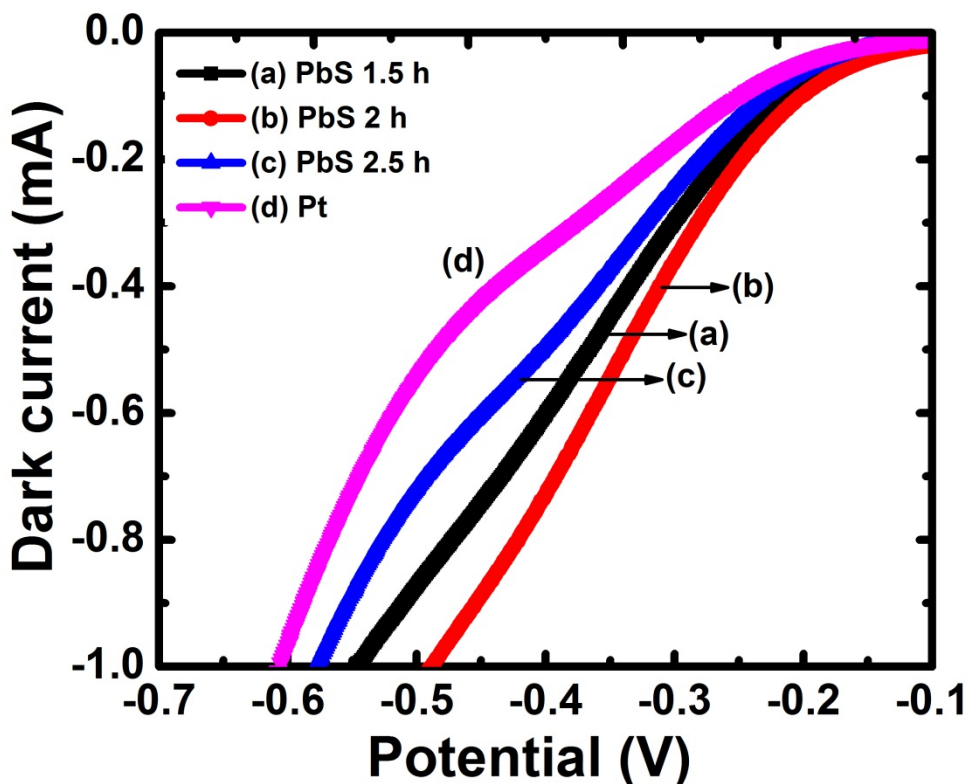


Fig. S1 Dark current Vs potential curves of QDSSCs with different counter electrodes under dark condition.

Cyclic voltammetry of PbS and Pt CEs:

In order to further investigate the redox process at polysulfide electrolyte/CE interface is studied by cyclic voltammetry using a three electrode system consisting of a working electrode, Pt wire counter electrode and SCE reference electrode. Fig. S2 shows the cyclic voltammograms of the PbS and Pt CEs carried out in a polysulfide electrolyte solution containing 0.1 M KCl, 0.1 M Na₂S, and 0.1 M S. Generally, the anodic peak represents the oxidation of S^{2-} ions to S_x^{2-} , while their cathodic peak corresponds to the reduction of S_x^{2-} to S^{2-} ions. In QDSSCs, the reduction peak current density value (J_{pc}) and the peak to peak separation (E_{pp}) are two important parameters are directly reflect the electrocatalytic ability of the CEs for S_x^{2-} reduction.³

Accordingly, the PbS 2 h CE shows a much higher current density relative to that of PbS 1.5 h, 2.5 h, and Pt CEs. Both PbS 1.5 h and 2.5 h show a considerable amount of reversibility with the shift of redox peaks and reduced current density. This suggests that the reduction rate of S_x^{2-} is higher on the PbS 2 h CE when compared to PbS 1.5 h, 2.5 h, and Pt CEs and tends to have a higher current density.⁴⁻⁶ The reduction peak for the Pt is inconspicuous, because the sulfur compounds heaped on the Pt surface resulting irreversibility and over potential towards polysulfide electrolyte. This results reveals that the PbS 2 h CE has a greater electrocatalytic activity and conductivity towards polysulfide electrolyte compared to the other CEs, which is due to the higher FF and low R_{ct}, in accordance with its excellent photovoltaic performance and EIS results. The EIS and CV results confirms that the PbS CE act an effectively in the polysulfide electrolyte.

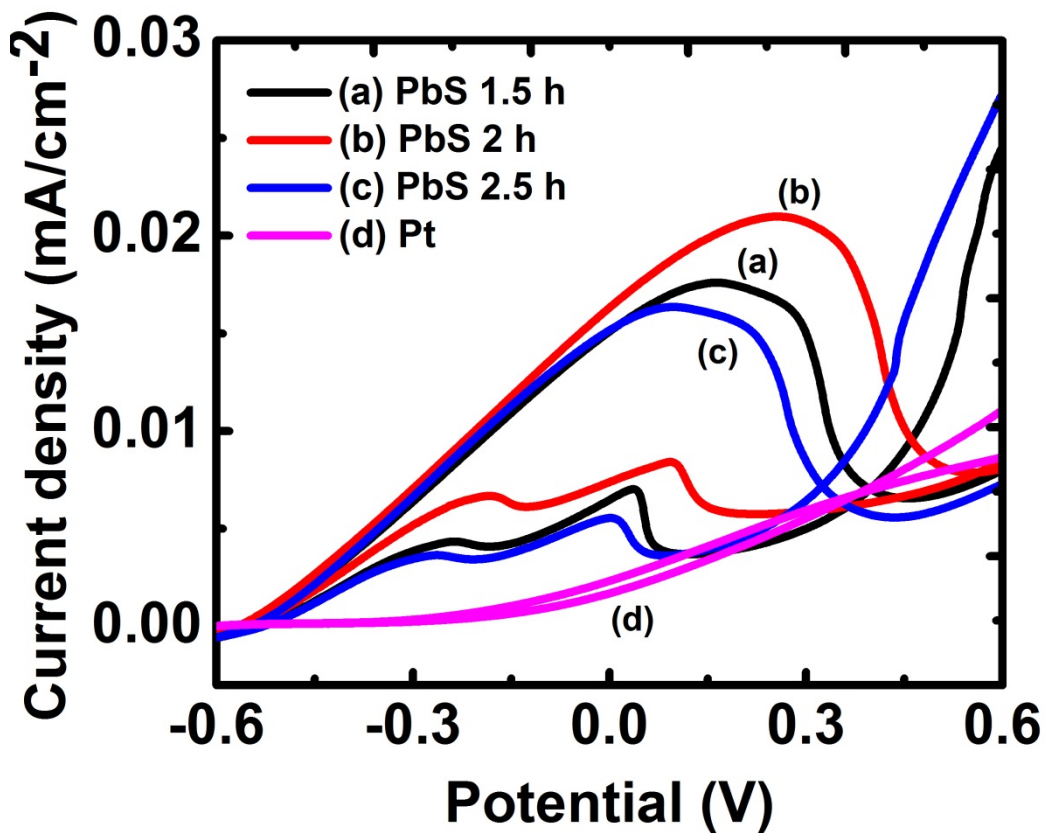


Fig. S2 Cyclic voltammograms of symmetrical cell based on PbS and Pt CEs at a scan rate of 50 mV

Effect of PbS CEs film thickness on performance of the QDSSCs

To further understand the dependence of short-circuit current density and fill factor on the thickness of PbS CEs, electrochemical impedance spectroscopy was also used to characterize the quantum-dot sensitized solar cells. Three cells fabricated from PbS CEs with thicknesses of 734 nm, 1.32 μ m, and 605 nm are shown in Fig. S3. Obviously, the decreased first semicircle in figure indicates the acceleration of the electron transfer at the CE/polysulfide electrolyte interface. This is consistent with the enhanced fill factor due to decreased series resistance in the

deposition time of PbS 2 h CE when compared to PbS 1.5 h, PbS 2.5 h, and Pt CEs. It was also observed that the 734 nm thickness of PbS 1.5 CE deposited on FTO substrate is constructed with crystal size of 7.5 nm, as shown in the inset figure a. when the film thickness is increased to 1.32 μm , the size of crystals grew to 7.5 to 11 nm (inset figure b.) Further increase in the thickness was not observed when the deposition time was increased over 2 h. which means the crystal surface microstructure disappeared and an uneven PbS was formed on the FTO substrate, as shown in the figure C. In fact we found that the energy conversion efficiency could be greatly improved with a PbS 2 h CE. In addition, the conversion efficiency could be also greatly improved by increasing current density. It can be concluded from the thickness of PbS 2 h, the crystal size of PbS gradually increased and their porosity declined with the increase in deposition time. This is mainly due to the aggregation of the crystal during deposition times.

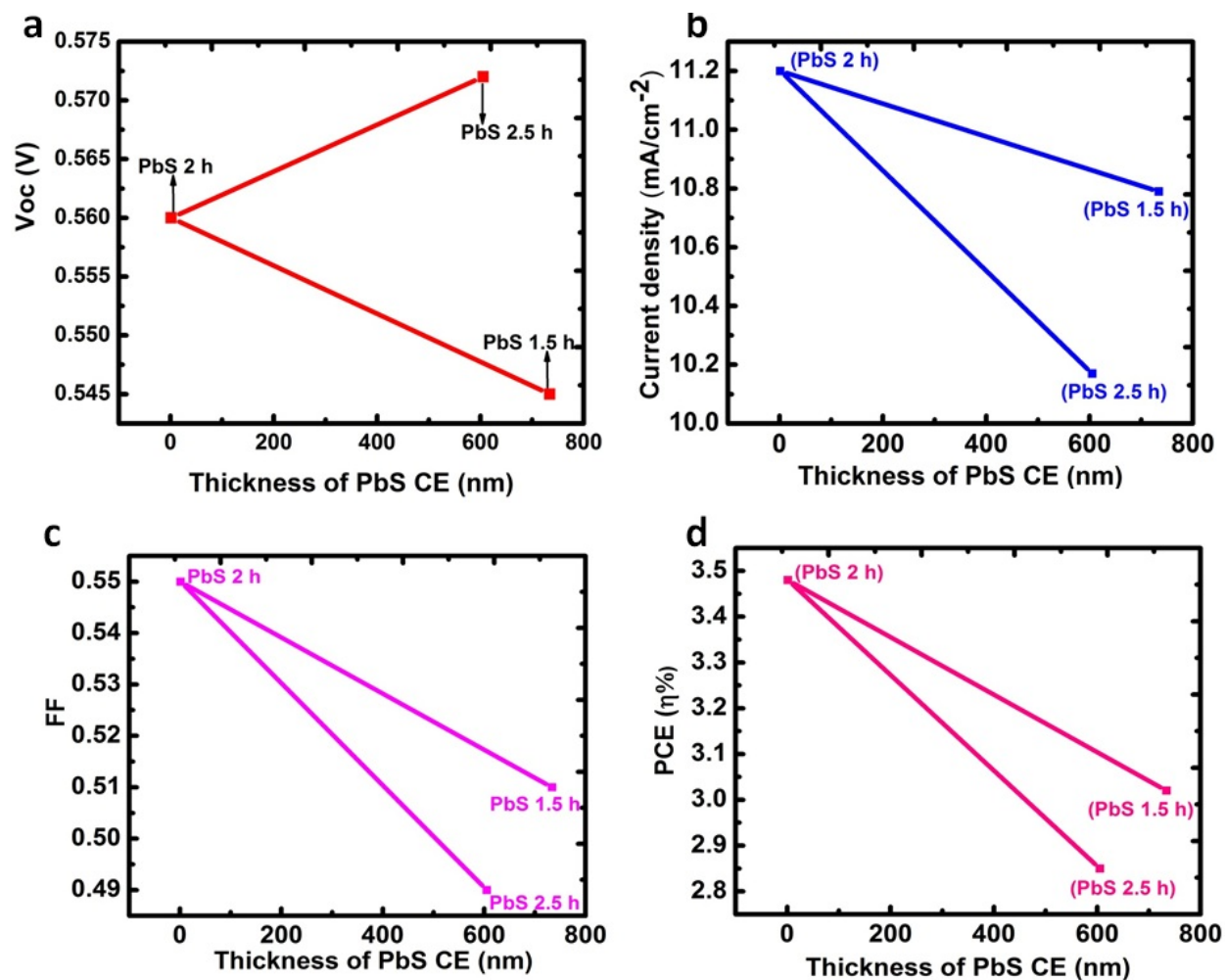


Fig. S3 Parameters of the quantum dot-sensitized solar cell using with different thickness as counter electrodes measured under AM 1.5 illumination. (a) Dependence of the open-circuit voltage on film thickness. (b) Dependence of the current density on film thickness. (c) Dependence of the fill factor on film thickness. (d) Dependence of the energy conversion efficiency on film thickness.

Effect of PbS CEs film thickness on sheet resistance:

The variation of sheet resistance of PbS CEs with the film thickness is clearly depicted in fig. S4. The sheet resistance (R_s) of the PbS 2 h CE decreased with the increase in the PbS 2 h

CE thickens and increase in the deposition time from 1.5 h to 2 h. The thickness range between 734 nm to 1.32 μm . According to the SEM micrographs, PbS 2 h CE has uniform surface morphology and good quality over the entire FTO substrate without any empty surface regions. Moreover, when the deposition time exceeded 2 h, the crystal surface microstructure disappeared and an uneven PbS was formed on the FTO substrate. [It is clear evidence from the figure 3c]. These results indicates that the conductivity of the PbS 2 h CE can be improved, which results higher current density and fill factor. These factors will clearly effecting on the performance of QDSSCs.

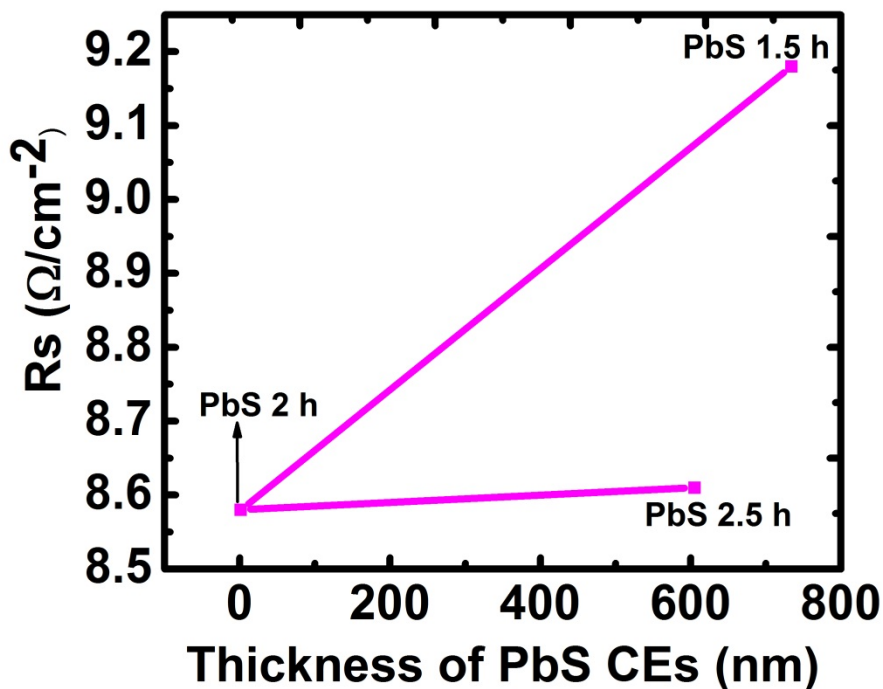


Fig. S4 the dependence of sheet resistance of PbS CEs on film thickness

References:

- 1 X. Xu, D. Huang, K. Cao, M. Wang, S. M. Zakeeruddin, and M. Gratzel, *Scientific Reports.*, 2013, **3**, 1489
- 2 E. Ramasamy, W. J. Lee, D. Y. Lee, J. S. Song, *Electrochemistry Communications.*, 2008, **10**, 1087–1089
- 3 J. D. Roy-Mayhew, D. J. Bozym, C. Punckt, and I. A. Aksay, *ACS Nano.*, 2010, **4**, 6203–6211.
- 4 J. G. Radich, R. Dwyer, and P. V. Kamat, *J. Phys. Chem. Lett.*, 2011, **2**, 2453-2460.
- 5 C. Justin Raj, K. Prabakar, A. Dennyson Savariraj, and K. Hee-Je, *Electrochim. Acta.*, 2013, **103**, 231.
- 6 X. H. Song, M. Q. Wang, J. P. Deng, Y. Ju, T. Y. Xing, J. J. Ding, Z. Yang and J. Y. Shao, *J. Power Sources.*, 2014, **269**, 661.