Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2015

Supplementary Information

Hierarchical I-P and I-N Porous Heterojunction in

Planar Perovskite Solar Cells

Hsueh-Chung Liao,^{a,b} Cheng-Si Tsao, *c Meng-Huan Jao,^a Jing-Jong Shyue,^d Che-Pu Hsu,^a Yu-Ching

Huang,^c Kuo-Yo Tian,^a Charn-Yin Chen,^c Chun-Jen Su,^e and Wei-Fang Su^{*a}

^a No. 1, Sec. 4, Roosevelt Road, Department of Materials Science and Engineering, National Taiwan University, Taipei 10617, Taiwan

Fax: +886 2 33664078; Tel: +886 2 33664078; E-mail: suwf@ntu.edu.tw

^b No.2-3, Ln. 66, Zhulin Rd., Yonghe Dist., New Taipei City 23441, Taiwan, FrontMaterials Co. Ltd.

^c No. 1000, Wenhua Road, Institute of Nuclear Energy Research, Longtan Township, Taoyuan County 32546, Taiwan

Tel: +886 3 4711400 ext. 3420; E-mail: <u>cstsao@iner.gov.tw</u>

^d No. 128, Academia Road, Section 2, Academia Sinica, Nankang, Taipei 115, Taiwan

^e No. 101, Hsin-An Road, National Synchrotron Radiation Research Center, Hsinchu 300-77, Taiwan

Effect of substrate on the GISAXS experiments

The substrate used in the GISAXS experiments was Si because of its flat surface (with very low roughness) and minor (negligible) contribution to the GISAXS background intensities.¹⁻³ However, the concern of substrate differences between solar cell device (FTO/TiO₂ or ITO/PEDOT:PSS) and GISAXS samples (Si) should be addressed for the morphological investigation. Hence, the GISAXS profiles of one-step and two-step processed perovskite obtained from different substrates (*i.e.* Si and Si / TiO₂) are shown in Figure S1. The preparation method of compact TiO₂ layer on the Si was identical to the solar cell device fabrication. Note that for the reduction of GISAXS profile, the background subtraction was performed according to the sample film transmission which can be obtained from the ratio of the specular beam intensities between sample on substrate and pure substrate in the identical GISAXS geometry.

Taking the compact TiO₂ as sample and Si as substrate, its GISAXS profile (black diamond) indicates that large number of uniform domain with size of 10 nm ~ 20 nm disperse on the surface. For the onestep method, the GISAXS profiles of the perovskite films on Si/TiO₂ or Si are almost the same. It implies that the TiO₂ ETM has no effect on the formation of pore structure. For the two-step method the perovskite on Si/TiO₂ substrates reveals subtly different GISAXS profile in low-*Q* region as compared to that of Si substrate. The GISAXS modeling shows that the domain size of fractal pore networks increases to $2R_g \sim 800$ nm when using the Si/TiO₂ substrate, while the volume fraction, fractal dimension and pore sizes remains similar to those of the Si substrate. Nevertheless, the domain sizes of pore networks using both substrates are still larger than layer thickness (~300 nm), indicating the pores aggregate into networks throughout the perovskite layer.



Figure S1. GISAXS profiles of TiO_2 compact layer, one-step and two-step processed perovskite on Si substrate and Si/TiO₂ substrate respectively. The profiles were reduced with background subtraction according to the sample film transmission, *i.e.* the ratio of the specular beam intensities between sample on substrate and pure substrate.⁴

Interface (Surface) area determined by Porod's law

A model-independent determination to the interface area S_v of pore structure between one-step and twostep processed perovskite can be approximated by Porod law

$$K = \lim_{Q \to \infty} [Q^4 \cdot I(Q)] = 2\pi (\Delta \rho)^2 S_{\nu} \qquad (S1)$$

The constant *K* is the asymptotic value obtained from the product of $Q^4I(Q)$ at the high-*Q* region. Due to the difficulty in determine the absolute contrast of scattering length density ($\Delta \rho$) in GISAXS configuration, herein we use the constant *K* to compare the relative interface area between one-step and two-step processed perovskite based on the identical scattering length density contrast ($\Delta \rho$). For determining the *K* value, the GISAXS intensity in the high-*Q* region can be approximated by^{1, 5}

$$I(Q) = KQ^{-4} + b \tag{S2}$$

Where b is the background value and K can be extracted from the intercept at Q =0. The plot of Q⁴I(Q) vs. Q⁴ is shown in Figure 2b in the manuscript. The extracted K values of one-step and two-step processed perovskite are 4.1×10^{-8} Å⁻⁴ and 1.3×10^{-7} Å⁻⁴ respectively.

GISAXS profiles of two-step processing of $\ensuremath{\text{PbI}}_2$ layer (step I) and perovskite layer

(step II)



Figure S2 GISAXS profiles of two-step processing of PbI₂ layer (step I) and perovskite layer (step II).

1D XRD pattern of PbI_2 and two-step processed perovskite



Figure S3 1D XRD pattern of PbI_2 and two-step processed perovskite layer. It shows that almost all the PbI_2 layer transforms into perovskite structure during the dip process (step II) with little residual PbI_2 .

- 1. H. C. Liao, C. S. Tsao, T. H. Lin, C. M. Chuang, C. Y. Chen, U. S. Jeng, C. H. Su, Y. F. Chen and W. F. Su, *J. Am. Chem. Soc.*, 2011, **133**, 13064-13073.
- 2. H.-C. Liao, C.-S. Tsao, Y.-T. Shao, S.-Y. Chang, Y.-C. Huang, C.-M. Chuang, T.-H. Lin, C.-Y. Chen, C.-J. Su, U. S. Jeng, Y.-F. Chen and W.-F. Su, *Energy Environ. Sci.*, 2013, **6**, 1938.
- H. C. Liao, C. S. Tsao, T. H. Lin, M. H. Jao, C. M. Chuang, S. Y. Chang, Y. C. Huang, Y. T. Shao, C. Y. Chen, C. J. Su, U. S. Jeng, Y. F. Chen and W. F. Su, *ACS Nano*, 2012, 6, 1657-1666.
- 4. H. C. Liao, C. S. Tsao, Y. T. Shao, S. Y. Chang, Y. C. Huang, C. M. Chuang, T. H. Lin, C. Y. Chen, C. J. Su, U. S. Jeng, Y. F. Chen and W. F. Su, *Energy Environ. Sci.*, 2013, **6**, 1938-1948.
- 5. G. Laudisio, R. K. Dash, J. P. Singer, G. Yushin, Y. Gogotsi and J. E. Fischer, *Langmuir*, 2006, **22**, 8945-8950.