

## Supporting Information

# Indium-tin-oxide nanorods for efficient light trapping in polymer solar cells†

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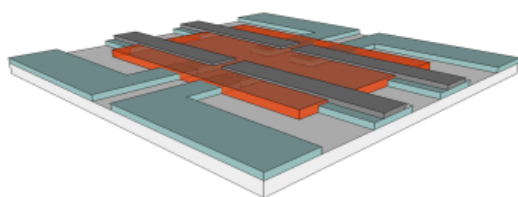
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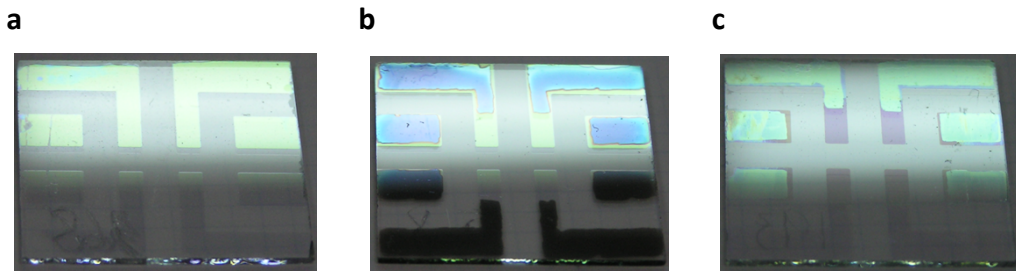
### **Preparation of ITO nanorods**

Commercial available ITO-coated glass substrates, purchased from Uni-onward Corp., were cleaned with acetone, IPA, and DI water before routine patterning procedures to make 2.5 cm × 2.5 cm substrates with patterns for 4 devices (Supplementary Figure S1). The pre-patterned substrates were cleaned and sent to a thermal evaporator for Al protective layer deposition. The Al protective layer was deposited on pre-patterned ITO-coated glass substrate through a metal mask under  $10^{-4}$ ~ $10^{-3}$  Pa with a deposition rate less than 0.2 Å/s. The metal mask has a pattern which makes the Al protective layer only being deposited on the area outside the active

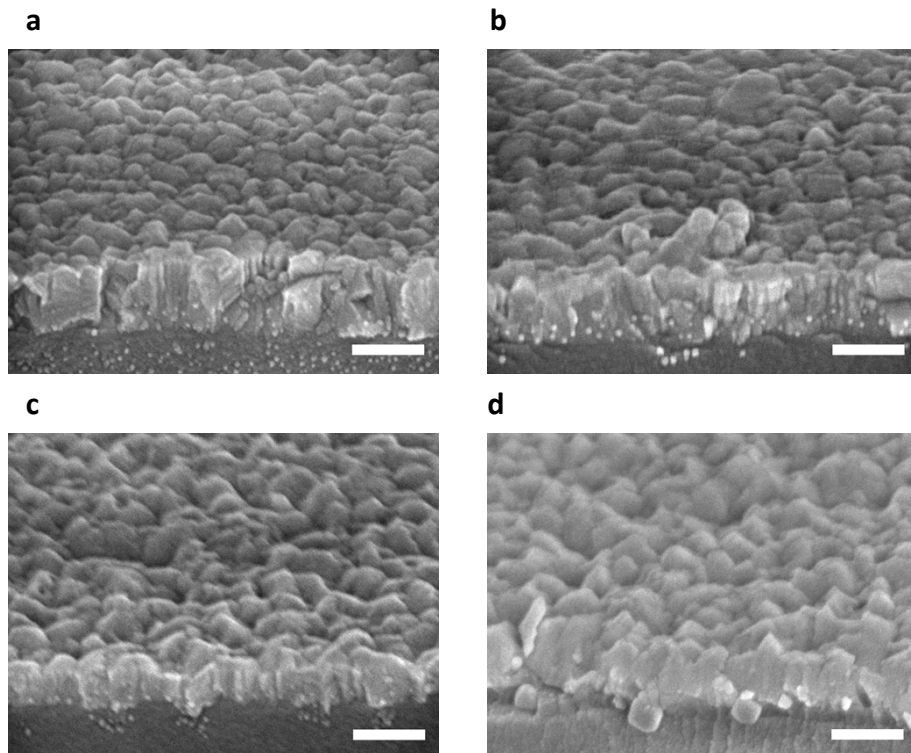
region. To fabricate ITO nanorods, the substrate with Al protective layer was submerged in phosphoric acid at 40° C for various times. The substrates etched for 10 min were selected for polymer solar cells fabrication. The regions with ITO nanorods become more transparent as compared with ITO film. Besides, when inspecting a substrate with a white reflective light as background, the color of the active areas was changed (Supplementary Figure S2). However, when the Al protective layer was not deposited, the ITO thickness decreases and the ITO roughness increases with increasing the phosphoric acid etching time (Supplementary Figure S3).



**Figure S1. The schematic illustration of a substrate with four devices on it.** The PEDOT:PSS was deposited as the hole transporting layer. The P3HT:PCBM blend was utilized as the photoactive layer and the Ca/Al was the cathode.



**Figure S2. The photographic images taken with a white reflective light as background. a.** Before Al protective layer deposition. **b.** After Al protective layer deposition. **c.** After phosphoric acid etching.

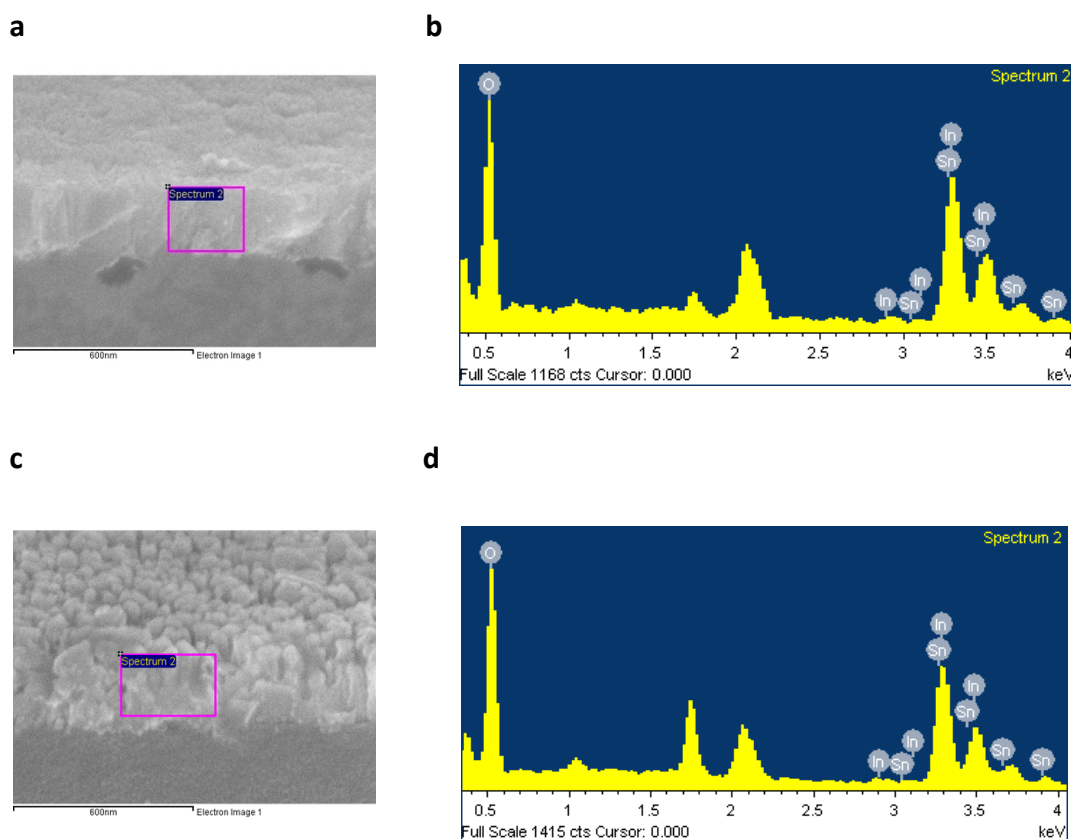


**Figure S3. The SEM images of ITO-coated glass substrates without Al protective layer. The phosphoric acid etching times at 50° C are a. 2 hr, b. 3 hr, c. 4 hr, and d. 5**

hr. The scale bar corresponds to 200 nm.

### Analysis of energy dispersive X-ray spectroscopy

Energy dispersive X-ray spectroscopy (EDS) was performed to understand the change in stoichiometry (Supplementary Figure S4). The atomic % of oxygen, indium, and tin in ITO film are 81.58%, 16.72%, and 1.70%. The atomic% of oxygen, indium, and tin in ITO nanorods are 83.17%, 15.17%, and 1.66%. The EDS spectrum indicate that the Sn/In ratio of the ITO film is 0.102, while the one of the ITO nanorods is 0.109. No remarkable change was found.



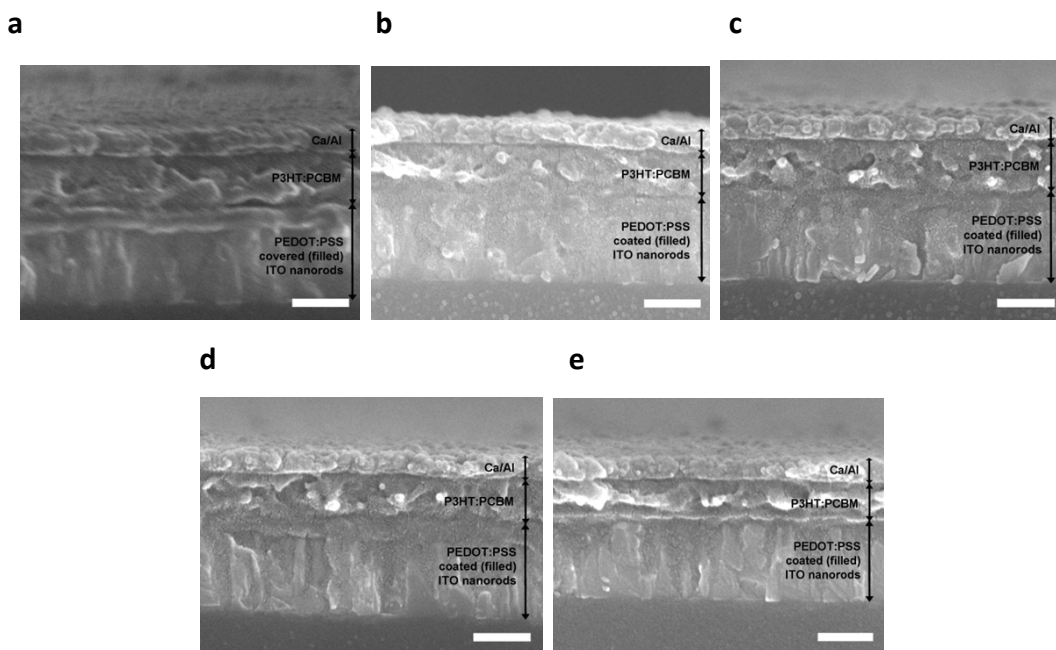
**Figure S4. The analysis of energy dispersive X-ray spectroscopy. a. ITO film. b. ITO nanorods.**

### **Spin-coating of PEDOT:PSS and blend of P3HT and PCBM**

We found that the spin-coating of pure PEDOT:PSS aqueous solution on ITO nanorods resulted in serious dewetting problem. Because of the dewetting properties of the nanostructured morphology, infiltration of PEDOT:PSS into gaps between ITO nanorods was incomplete which might cause shunt at the crests. Therefore, to prevent poor PEDOT:PSS infiltration, the PEDOT:PSS was blended with isopropanol and Triton X-100 for better wetting properties. The blending volume ratio is PEDOT:PSS : IPA : Triton X-100 = 50 : 50 : 1. Indeed, we successfully demonstrated that the wetting problem was resolved, and the blend solution of PEDOT:PSS, IPA, and Triton X-100 can fill the gaps between nanorods or conformally cover on the nanorods by simply adjusting the spin coating speed. The gaps between PEDOT:PSS coated ITO nanorods were diminished as compared with the ones of ITO nanorods. Besides, for ITO nanorods with small spacing, even the PEDOT:PSS was spin coated with highest speed, PEDOT:PSS still rests between nanorods (Fig. 3e). The depths of the valleys between these PEDOT:PSS coated (conformal) ITO nanorods are in the range of 140 to 200nm.

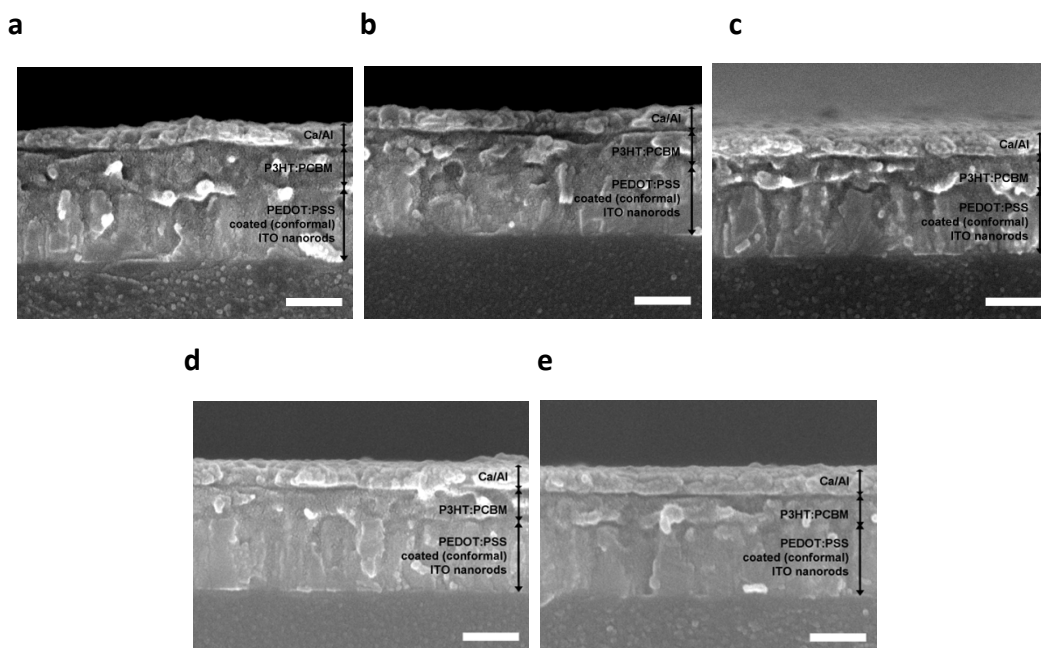
As for the deposition of photoactive layer, dewetting problem was not observed. The blend solution of P3HT and PCBM was prepared in dichlorobenzene because of

it high boiling point. Both the concentrations of P3HT and PCBM are 20 mg/ml. The blend solution can be deposited on the PEDOT:PSS with flat surface (Supplementary Figure S5) and on the PEDOT:PSS layer conformally coated on the ITO nanorods (Supplementary Figure S6). These images demonstrate that not only the blend solution of PEDOT:PSS : IPA : Triton X-100 but also the blend solution of P3HT : PCBM can infiltrate the gaps between ITO nanorods. The thickness of the photoactive layer can be controlled by spin coating speed.



**Figure S5. The SEM images of Device B with various photoactive layer**

**thicknesses. a.** 180 nm. **b.** 170 nm. **c.** 160 nm. **d.** 140 nm. **e.** 130 nm. The scale bar corresponds to 200 nm.

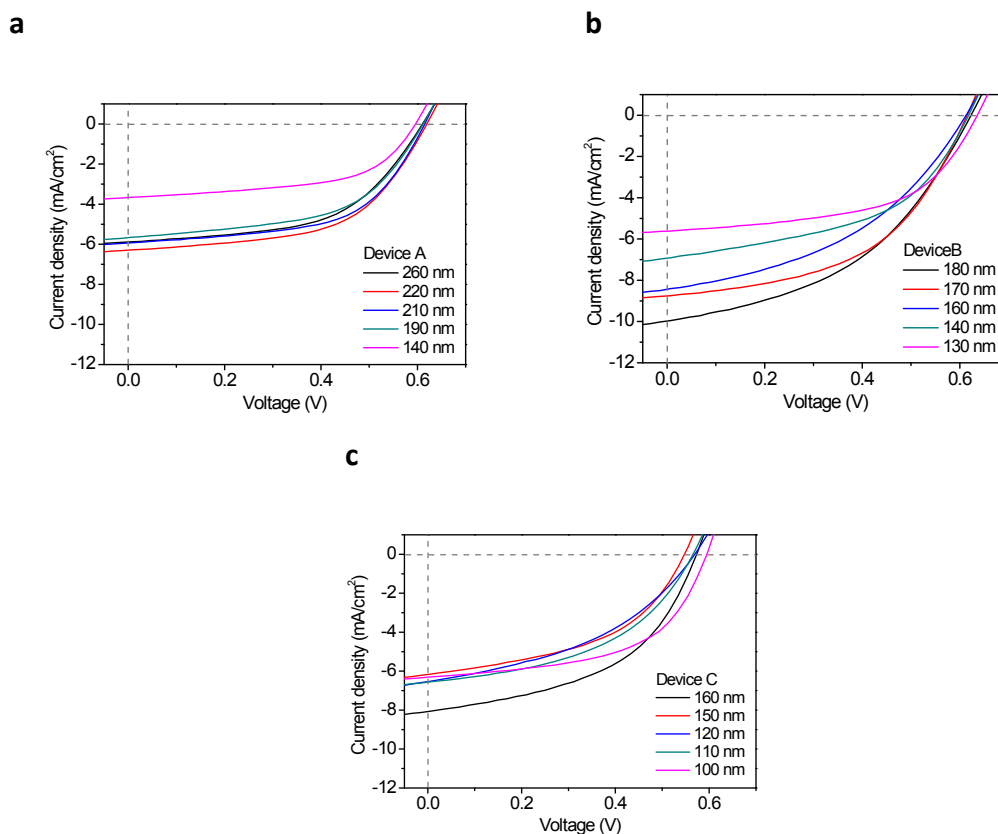


**Figure S6. The SEM images of Device C with various photoactive layer**

**thicknesses. a. 160 nm. b. 150 nm. c. 120 nm. d. 110 nm. e. 100 nm.** The scale bar corresponds to 200 nm.

### Device performance with various thicknesses

By adjusting the spin coating speed, Device A, B, and C were made with various photoactive layer thicknesses. The thicknesses of the photoactive layers are determined by estimating the distance between cathode and PEDOT:PSS. The  $J-V$  curves of devices under illumination were shown in Supplementary Figure S7.



**Figure S7. The  $J-V$  curves of Device A, B, and C with various photoactive layer thicknesses.**