

## Electronic supplementary information (ESI)

### Enhanced Photovoltaic Performance of Perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ Solar Cells with Freestanding $\text{TiO}_2$ Nanotube Array Films

*Xianfeng Gao, Jianyang Li, Joel Baker, Yang Hou, Dongsheng Guan, Junhong Chen, Chris Yuan\**

Department of Mechanical Engineering, University of Wisconsin Milwaukee, Wisconsin, 53211, United States

#### EXPERIMENT

##### *Free standing $\text{TiO}_2$ nanotube array fabrication*

Ti foils (99.5% purity, 0.25 mm thick, Alfa Aesar) were degreased by sonicating in acetone for 15 minutes followed by rinsing in de-ionized water prior to electrochemical anodization. The electrolyte was ethylene glycol (EG) containing 0.3 wt%  $\text{NH}_4\text{F}$  and 0.6 vol%  $\text{H}_2\text{O}$ . To avoid top end bundling and get stable free standing nanotube arrays, two-step anodization was used. The Ti foil was then anodized under 70 V for three hours, followed by ultrasonic washing in deionized water to completely remove the oxidation film and leave an ordered concave structure. Following that process anodization was performed under the same voltage for various times, generating nanotube arrays with controlled length (2.3 $\mu\text{m}$ , 4.8 $\mu\text{m}$ , 9.4 $\mu\text{m}$ ). The obtained film was then annealed at 450 °C for 2 hours. To get free standing  $\text{TiO}_2$  nanotube arrays, the modified detached method was used according to previous research.<sup>1</sup> The Ti foil was transferred back to the electrochemical cell and held at 12 V for 30 minutes and then at 100 V for another 30 minutes. After the final anodization, the sample was washed in de-ionized water. The thin anatase  $\text{TiO}_2$  layer was self-detached from substrate during the drying process.

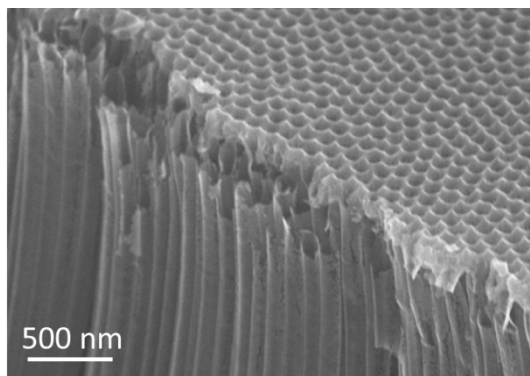
##### *Device fabrication*

FTO-coated glass was cleaned by acetone, ethanol and water, and subjected to an  $\text{O}_3$ /ultraviolet treatment for 30 minutes. The FTO layer was first covered with 0.1 M Ti(IV) bis(ethyl acetoacetato)-diisopropoxide in 1-butanol solution by spin-coating and then heated at 500 °C for 0.5h. Free standing  $\text{TiO}_2$  nanotube array film was transferred to the obtained substrate which was covered by a thin layer  $\text{TiO}_2$  nanoparticle paste as detailed previously.<sup>2</sup> The  $\text{TiO}_2$  nanotube electrode was then placed in an oven at 500 °C for 0.5 h.  $\text{PbI}_2$  was deposited into the  $\text{TiO}_2$  nanotube electrodes by spin coating at 6500 rpm for 5s and dried at 70 °C for 30 minutes. A 1M  $\text{PbI}_2$  solution in N,N-dimethylformamide was used. After cooling to room temperature, the electrodes were immersed in a solution of  $\text{CH}_3\text{NH}_3\text{I}$  in 2-propanol (30mgml<sup>-1</sup>) for 20 minutes,

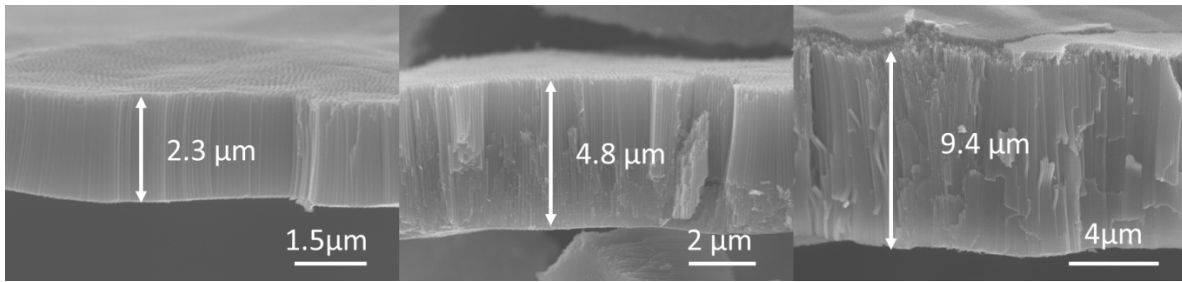
and then rinsed with 2-propanol and dried at 70 °C for 30 minutes in Ar.  $\text{CH}_3\text{NH}_3\text{I}$  is synthesized according to procedures from a previous report.<sup>3</sup> Note that relatively high concentrations of  $\text{CH}_3\text{NH}_3\text{I}$  are necessary for small size perovskite  $\text{CH}_3\text{NH}_3\text{PbI}_3$  formation inside the tubes. Finally, a 25  $\mu\text{m}$  thick Surlyn frame was sandwiched between the open-pore side of the membrane and a platinized FTO. Electrolyte was comprised of 0.08 M LiI, 0.04 M  $\text{I}_2$ , 0.05 M tBP (4-tert-butylpyridine), and 0.005 M urea in ethyl acetate. The reference  $\text{TiO}_2$  nanoparticle electrode composed of 20-nm-sized particles (Dyesol 18NTR) was prepared by a doctor blading technique with all other experimental parameters left the same.

#### *Device characterization*

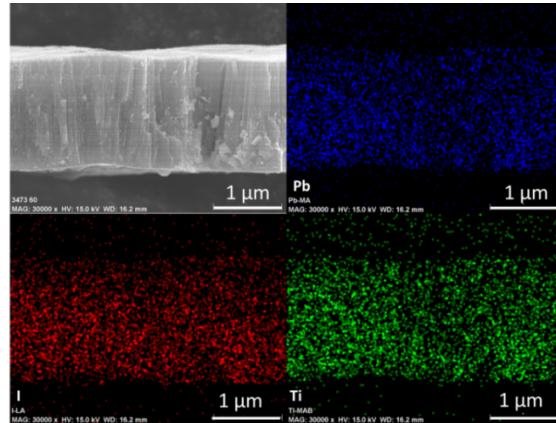
Hitachi S-4800 scanning electron microscopy (SEM) and Hitachi H9000NAR transmission electron microscopy (TEM) were used to characterize the morphology of the nanotube electrode. The composition of the obtained material was examined by Energy-dispersive X-ray spectroscopy (EDS), and the crystal structure was further analyzed by X-ray diffraction spectrum (XRD). Light absorbance of the photoelectrode was characterized with an Ocean Optics UV-VIS Spectrometer (SD2000 fiber optics). The J-V properties of  $\text{TiO}_2$  nanotube based perovskite solar cells were tested using a Keithley 2420 source meter under illumination of  $100\text{mW}/\text{cm}^2$  by an oriel solar simulator. J-V curve under reverse scan condition was selected to evaluate the performance of the devices. Long delaying time ( $\sim 80\text{ms}$ ) between each testing step was used to avoid the overshooting of photo efficiency. Incident photon to charge carrier efficiency (IPCE) measurement was performed with Newport measurement kit with 300W Xe lamp source. The wavelength of light was tuned with a Newport CS260 monochromator. Photovoltage decay measurements were performed by a CHI660D Electrochemical Analyzer.



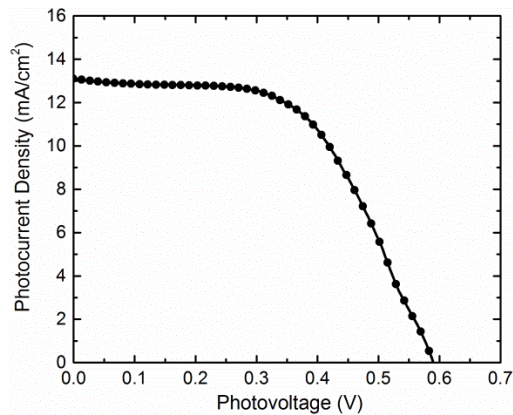
**Figure S1.** Cross section image of free standing  $\text{TiO}_2$  nanotube array film



**Figure S2.** Cross section images of free standing  $\text{TiO}_2$  nanotube array film with varied thickness



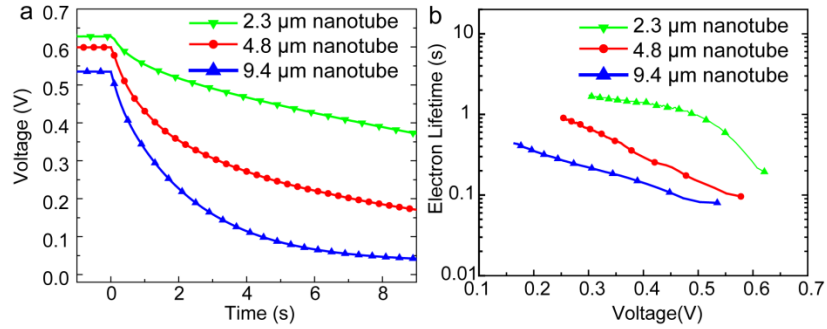
**Figure S3.** EDS mapping of cross section  $\text{TiO}_2$  nanotube with  $\text{CH}_3\text{NH}_3\text{PbI}_3$  deposition



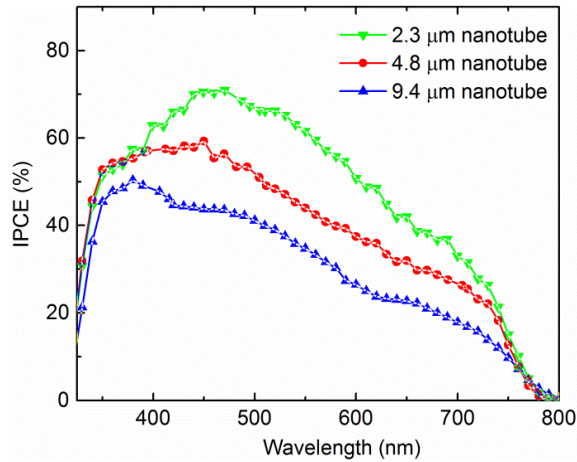
**Figure S4.** J-V curve of perovskite solar cell with  $4.8 \mu\text{m}$  free standing  $\text{TiO}_2$  nanotube array film. Measurement was carried out under forward scan condition (from 0V to 0.8V).

**Table S1.** Performance comparison of perovskite solar cell with  $4.8 \mu\text{m}$  free standing  $\text{TiO}_2$  nanotube array measured under different scan directions.

$4.8 \mu\text{m}$	$V_{oc}$ [V]	$J_{sc}$ [ $\text{mAcm}^{-2}$ ]	FF	$\eta$ [%]
forward	0.59	13.2	0.562	4.38
reverse	0.60	13.1	0.568	4.46



**Figure S5.** Open-circuit voltage decay (a) and lifetimes (b) of the perovskite solar cell with varied thickness TNT films.



**Figure S6.** IPCE spectra of the perovskite solar cell with varied thickness TNT films.

### Reference

1. H. M. Ouyang, G. T. Fei, Y. Zhang, H. Su, Z. Jin, S. H. Xu and L. De Zhang, *Journal of Materials Chemistry C*, 2013, **1**, 7498-7506.
2. X. Gao, D. Guan, J. Huo, J. Chen and C. Yuan, *Nanoscale*, 2013, **5**, 10438-10446.
3. J. H. Im, C. R. Lee, J. W. Lee, S. W. Park and N. G. Park, *Nanoscale*, 2011, **3**, 4088-4093.