

Solid-State Mesostructured Perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ Solar Cells: Charge Transport, Recombination, and Diffusion Length

Yixin Zhao, Alexandre M. Nardes, and Kai Zhu*

Chemical and Materials Science Center, National Renewable Energy Laboratory, Golden, Colorado 80401

Experimental Method

Transparent conducting substrate. Fluorine-doped transparent conducting SnO_2 -coated glass substrate (FTO; TEC15, Hartford, USA) was pre-patterned by etching with Zn powder and 25 wt% HCl solution for about two min. The patterned FTO substrate was then cleaned by soaking in 5 wt% NaOH in alcohol for 16 h and then rinsing it sequentially with deionized (DI) water and ethanol. The cleaned FTO substrate was subsequently coated with a compact TiO_2 layer by spray pyrolysis using 0.2 M Ti(IV) bis(ethyl acetoacetate)-diisopropoxide in 1-butanol solution at 450°C , followed by annealing at 450°C for 1 h.¹

Mesoporous TiO_2 film. The 20-nm-sized TiO_2 nanoparticles were synthesized by following previous reports.²⁻³ Various TiO_2 pastes with different weight percentages (3–18 wt%) of the 20-nm TiO_2 nanoparticles mixed with terpineol and ethyl cellulose were screen-printed on the patterned FTO substrates to produce TiO_2 films with average film thickness ranging from 240–1650 nm. The thickness is controlled by using TiO_2 paste with different weight percentage of TiO_2 nanoparticles. The emulsion thicknesses of the screens were also adjusted. The printed mesoporous TiO_2 film was annealed at 500°C for 0.5 h. The TiO_2 films were then soaked in 0.04 M TiCl_4 solution at 65°C for 0.5 h, followed by rinsing with DI water and ethanol, and finally dried under N_2 . These TiCl_4 -treated TiO_2 films were annealed again at 500°C for 0.5 h before the deposition of perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ absorber or uptake of Z907 dye molecules.

Device fabrication. For perovskite solar cells, the perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ coating was done by spin coating as detailed in our previous report.⁴ In brief, the perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ was deposited on the mesoporous TiO_2 film by spin coating with a stoichiometric $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 solution in γ -butyrolactone. $\text{CH}_3\text{NH}_3\text{I}$ was synthesized by reacting methylamine (33 wt% ethanol solution) and hydroiodic acid (57 wt% in water, Aldrich) with the molar ratio of 1.2:1 in an ice bath for 2 h with stirring. The precipitate was first dried by a rotary evaporator, followed by repeated washing and centrifuging with ethyl acetate until no yellow residue remains, and finally dried under vacuum. 1.157 g PbI_2 and 0.395 g $\text{CH}_3\text{NH}_3\text{I}$ were dissolved in 2.0 mL γ -butyrolactone solution at 60°C . The clear

perovskite precursor solution was first spread on the TiO₂ substrate for 5 s and then was spun at 2000 rpm for 30 s in ambient condition. The deposited CH₃NH₃PbI₃ film was finally dried on a hotplate at 100°C for 5 min. For dye-sensitized solar cells, the TiO₂ films were immersed in *tert*-butyl alcohol/acetonitrile (1:1, v/v) containing 0.3 mM Ru(4,4'-dicarboxylic acid-2,2'-bipyridine)(4,4'-dinonyl-2,2'-bipyridine)(NCS)₂ (Z907) for 16 h at room temperature.

For both perovskite solar cells and dye-sensitized solar cells, a hole transport material (HTM) solution was spin-coated on the sensitized TiO₂ electrodes at 4000 rpm for 30 s. The HTM solution consists of 0.15 M 2,2',7,7'-tetrakis-(*N,N*-di-*p*-methoxyphenyl-amine)-9,9'-spirobifluorene (spiro-MeOTAD), 0.05 M bis(trifluoromethane)sulfonimide lithium salt (Li-TFSi), and 0.18 M 4-*tert*-butylpyridine (tBP) in chlorobenzene/acetonitrile (10:1, v/v) solution. Finally, a 150-nm-thick Ag layer was deposited on the HTM layer by thermal evaporation. The active area of each device was about 0.15–0.28 cm².

Characterization. The crystal structures of the perovskite films were measured by X-ray diffraction (XRD, Rigaku D/Max 2200 diffractometer with Cu K_α radiation). The absorption spectra of the perovskite films were characterized by an UV/Vis-NIR spectrophotometer (Cary-6000i). The photocurrent–voltage characteristic of solid-state mesostructured perovskite cells and dye-sensitized solar cells were measured with a Keithley 2400 source meter under the simulated AM 1.5G illumination (100 mW/cm²; Oriel Sol3A Class AAA Solar Simulator). The performance data of perovskite solar cells are representative from 12–20 cells (unless otherwise stated) for each TiO₂ film thickness. Charge transport and recombination properties of the perovskite sensitized cells were measured by intensity-modulated photocurrent and photovoltage spectroscopies as described previously.⁵

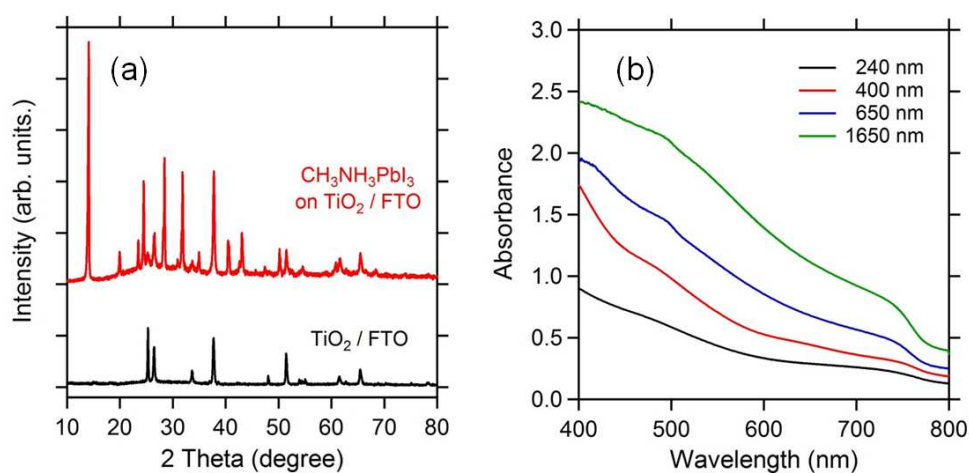


Figure S1. (a) X-ray diffraction patterns of the TiO₂/FTO substrate and perovskite CH₃NH₃PbI₃ deposited on the TiO₂/FTO substrate. (b) UV-vis absorption spectra of perovskite CH₃NH₃PbI₃ as a function of TiO₂ film thickness.

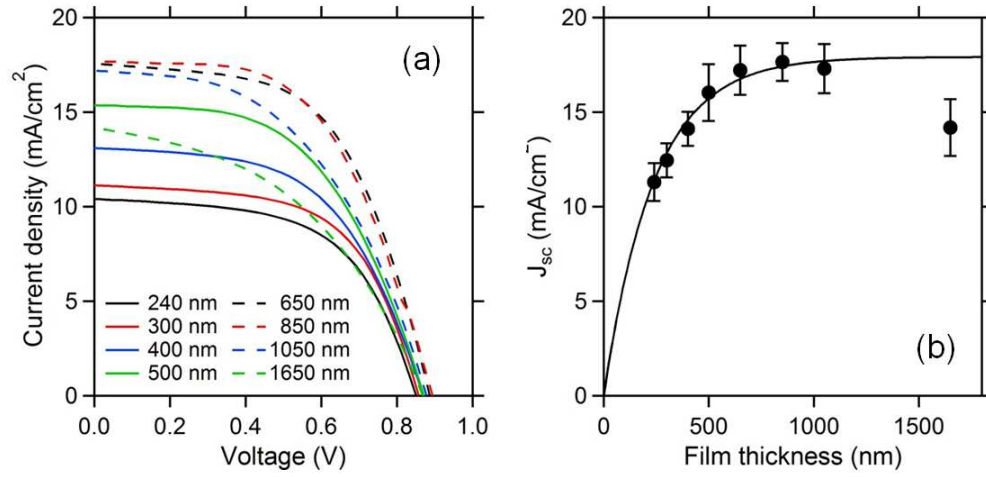


Figure S2. (a) Effect of TiO₂ film thickness on the J - V curves of mesostructured perovskite CH₃NH₃PbI₃ solar cells. (b) Dependence of J_{sc} on the TiO₂ film thickness. The error bars represent the measurements from 12–20 cells. The solid line in (b) is a fitting to a simple model $J_{sc} \propto 1 - \exp(-\alpha d)$ assuming constant charge-collection efficiency for all thickness (d) and an effective absorption coefficient (α). This simple model fits well for all samples except for the one with the thickest TiO₂ film (1.65 μ m). The effective absorption length ($1/\alpha$) from the fitting is about 250 nm.

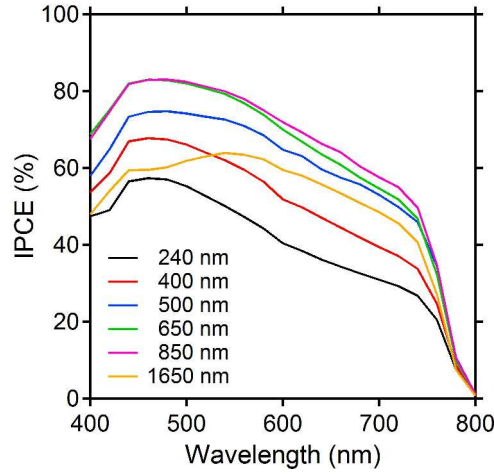


Figure S3. Effect of TiO₂ film thickness on the IPCE spectra of mesostructured perovskite CH₃NH₃PbI₃ solar cells.

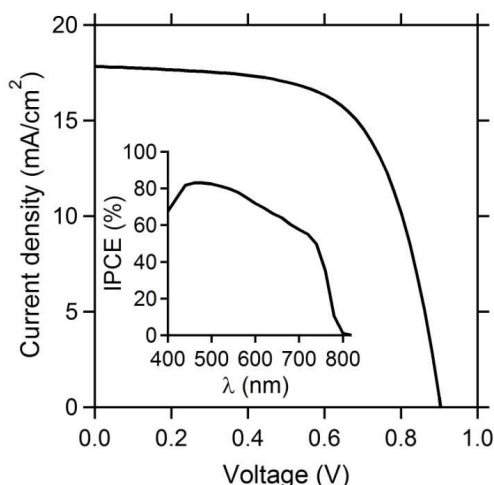


Figure S4. J - V and IPCE curves of an optimized solid-state mesostructured perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ solar cell using a 650-nm TiO_2 film. The cell efficiency is 10.3% with a J_{sc} of 17.8 mA/cm^2 , V_{oc} of 0.90 V, and FF of 0.64.

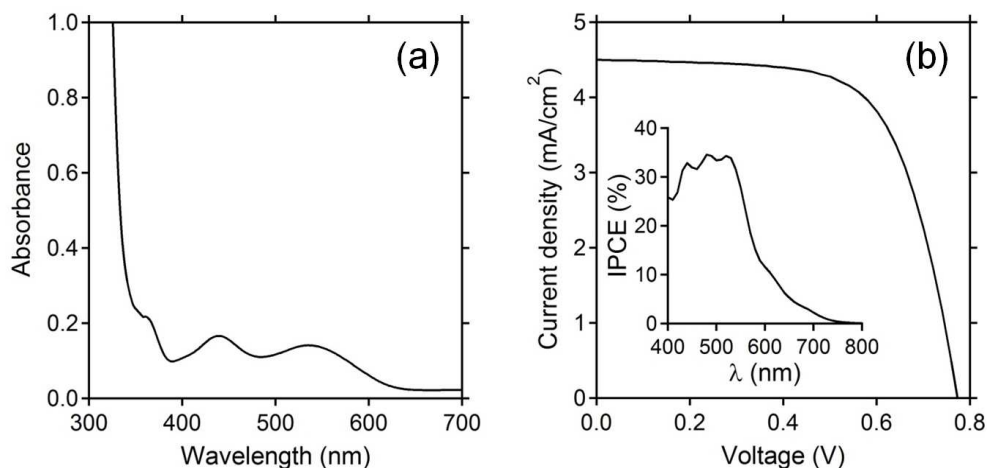


Figure S5. (a) UV-vis absorption spectrum and (b) J - V (inset: IPCE) of solid-state Z907 dye-sensitized solar cells using 650-nm-thick TiO_2 films.

REFERENCES

- (1). Jang, S. R.; Zhu, K.; Ko, M. J.; Kim, K.; Kim, C.; Park, N. G.; Frank, A. J. Voltage-enhancement mechanisms of an organic dye in high open-circuit voltage solid-state dye-sensitized solar cells. *ACS Nano* **2011**, 5, 8267–8274.
- (2). Neale, N. R.; Frank, A. J. Size and shape control of nanocrystallites in mesoporous TiO_2 films. *J. Mater. Chem.* **2007**, 17, 3216–3221.
- (3). Ito, S.; Murakami, T. N.; Comte, P.; Liska, P.; Gratzel, C.; Nazeeruddin, M. K.; Gratzel, M. Fabrication of thin film dye sensitized solar cells with solar to electric power conversion efficiency over 10%. *Thin Solid Films* **2008**, 516, 4613–4619.
- (4). Zhao, Y.; Zhu, K. Charge transport and recombination in perovskite $(\text{CH}_3\text{NH}_3)\text{PbI}_3$ sensitized TiO_2 solar cells. *J. Phys. Chem. Lett.* **2013**, 4, 2880–2884.
- (5). Zhu, K.; Kopidakis, N.; Neale, N. R.; van de Lagemaat, J.; Frank, A. J. Influence of surface area on charge transport and recombination in dye-sensitized TiO_2 solar cells. *J. Phys. Chem. B* **2006**, 110, 25174–25180.