

Thermally-activated recombination in one component of $(\text{CH}_3\text{NH}_3)\text{PbI}_3$ / TiO_2 observed by photocurrent spectroscopy

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Preparation of $\text{CH}_3\text{NH}_3\text{I}$. 33 wt% methylamine ethanol solution (Aldrich, $D_{25^\circ\text{C}} = 0.756$ g/mL, 28.3 mL, 0.228 mol) and 57 wt% hydroiodic acid in water (Aldrich, $D_{25^\circ\text{C}} = 1.701$ g/mL, 25.0 mL, 0.189 mol) containing hydrophosphous acid as a stabilizer were mixed and stirred at 0°C to form a clear solution. The solution was rotavapped down to form white precipitate and dried. The solid was washed three cycles by diethyl ether and was then vacuum dried (Yield = 89%).

Mesoporous TiO_2 and ZrO_2 Thin Films on FTO Substrate. The procedure has been described in a previous publication.¹ Briefly, 10 mL titanium(IV) isopropoxide (Aldrich, $\geq 97\%$) was added dropwise to 60 mL di water with 0.42 mL HNO_3 (70% V/V). The solution was heated to $\sim 95^\circ\text{C}$ and the volume was reduced to ~ 20 mL (~ 160 g/L in TiO_2 concentration). The solution was put in an acid digestion bomb and autoclaved at 200°C for 12 hours. The resulting product was opaque white in appearance and 0.9 g carbowax (Polyethyleneglycol Bisphenol A Epichlorohydrin Copolymer 15,000-20,000 Da, Aldrich) was added. The TiO_2 paste was “doctor-bladed” onto a precleaned fluorine doped tin oxide (FTO, $15 \Omega/\square$, Hartford Glass) substrate using Scotch Tape™ as the spacer, dried, and sintered in a tube furnace at 450°C under constant oxygen flow for 30 minutes. Mesoporous ZrO_2 thin films were made in a similar way except that Zr(IV) propoxide (70% in 1-propanol) was used as the precursor.

Preparation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ Substrates. 40.3% in weight perovskite solution was prepared by adding 0.979 g $\text{CH}_3\text{NH}_3\text{I}$ and 2.864 g PbI_2 (Aldrich, 99%) in 5 mL γ -butyrolactone (Aldrich, $\geq 99\%$) and stirred under argon at 60°C overnight. The solution was filtrated through a $0.22 \mu\text{m}$ PVDF syringe filter (MILLEX®GV). The resulting coating solution was spread on the substrates, allowed to wait for 1 minute, and spun coat on FTO substrate (1a) or mesoporous TiO_2 and ZrO_2 on FTO substrates (1b) for 45 seconds at speed of 4000 rpm. The coated slides were annealed at 100°C for 30 minutes and the color turned from light yellow to black.

X-Ray Diffraction of $\text{CH}_3\text{NH}_3\text{PbI}_3$ in mesoporous TiO_2 . In order to verify that the PbI_2 used to synthesize $(\text{CH}_3\text{NH}_3)\text{PbI}_3$ was fully reacted and $(\text{CH}_3\text{NH}_3)\text{PbI}_3$ was not decomposed, x-ray diffraction was performed on a sample of $(\text{CH}_3\text{NH}_3)\text{PbI}_3$ / mesoporous TiO_2 . Data were collected using a Bruker D8 diffractometer equipped with $\text{Cu K}\alpha$ radiation ($\lambda_1 = 1.54056 \text{ \AA}$, $\lambda_2 = 1.54439 \text{ \AA}$) and a LynxEye detector. This data is shown in Fig. S1, along with data collected on powdered PbI_2 . It is clear from the complete absence of any peaks in the former pattern near many values of 2θ where strong reflections occur in the latter pattern that no significant fraction of PbI_2 exists in the $(\text{CH}_3\text{NH}_3)\text{PbI}_3$ sample.

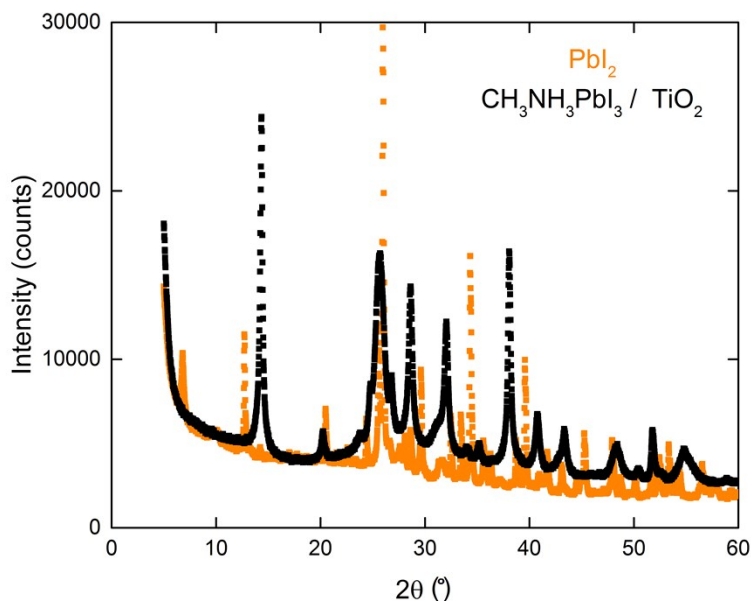


Fig. S1 X-ray diffraction patterns of powdered PbI₂ and a sample of (CH₃NH₃)PbI₃ in mesoporous TiO₂

Preparation of Device with Planar CH₃NH₃PbI₃ and TiO₂ Blocking Layer. A dense, compact TiO₂ layer was deposited on FTO glass substrates (Hartford Glass, Inc.) in the following way. A 0.15 M solution of titanium(IV) isopropoxide (Aldrich, ≥ 97%) in 2-propanol was spin-coated onto the substrate at 2000 RPM, followed by heating of the substrate at 110 °C for 10 minutes. The previous step was repeated twice with a 0.3 M solution followed by heating at 450 °C for 30 minutes. (CH₃NH₃)PbI₃ was deposited onto the FTO/blocking layer substrates according a variation on the method of Gratzel et al.² Briefly, a 1 M suspension of PbI₂ in dimethylformamide (DMF) which had been heated to 70 °C was spin-coated at 3000 RPM onto the FTO and blocking layer substrate which had also been preheated to 70 °C. This sample was then annealed for 30 minutes on a hotplate at 70 °C. The sample was then swirled in a 100 mg/ml solution of CH₃NH₃I in 2-propanol for 20 seconds. Drying the sample at 75 °C on a hotplate caused an immediate color change to homogenous dark brown. A solution of 10 mg/ml CH₃NH₃I and 1% in weight PEDOT:PSS (Aldrich, from dry pellets) in 2-propanol was spin-coated onto the sample at 2000 RPM in order to create a hole-transport layer. The sample was compressed against another piece of FTO glass and sealed with glue in order to create a complete photovoltaic device.

Device Measurement. Photocurrent measurements were conducted by mounting the samples in a bespoke probe which was inserted into a Quantum Design Physical Properties Measurement System (PPMS) in order to achieve precise control of the sample's temperature. A ~10 nm spectral band was selected from a white light source using a monochromator and used to illuminate the sample via an optical fiber. Samples were measured over the wavelength range $\lambda = 350\text{-}1100$ nm at each temperature, beginning with $\lambda = 350$ nm. Scans were performed at a series of decreasing temperatures, beginning at $T = 300$ K. A fraction of the light exiting the monochromator was directed into an Ophir photodiode in order to normalize measured photocurrents on an per-incident-Watt basis. The light

intensity arriving at the sample varied with wavelength and did not exceed 25 nW cm^{-2} at any wavelength. The output of the monochromator was mechanically chopped at 315 Hz and filtered for harmonics. Measurement of the photocurrent was accomplished by measuring the voltage across a resistor ($R = 9.8 \text{ k}\Omega$ or $980 \text{ k}\Omega$) connected across the terminals of the device using a Stanford Research Systems SRS830 lock-in amplifier.³

Comparison of Devices with Mesoporous TiO_2 and TiO_2 blocking layer. In order to verify that the appearance of two features in the photocurrent spectra of samples containing a mesoporous oxide matrix depends on infiltration of $(\text{CH}_3\text{NH}_3)\text{PbI}_3$ into the matrix, photocurrent measurements were performed on a device containing a dense, compact TiO_2 layer, but no mesoporous matrix. This spectra was collected at room temperature, with optical chopping at 50 Hz, using the SRS830 in current mode. In Fig. S2 this spectrum is compared with the $T = 300 \text{ K}$ spectrum of the mesoporous TiO_2 device described in the main text. It clear from this comparison that the presence of compact TiO_2 adjacent to a planar $(\text{CH}_3\text{NH}_3)\text{PbI}_3$ is insufficient to induce the appearance of two spectral components.

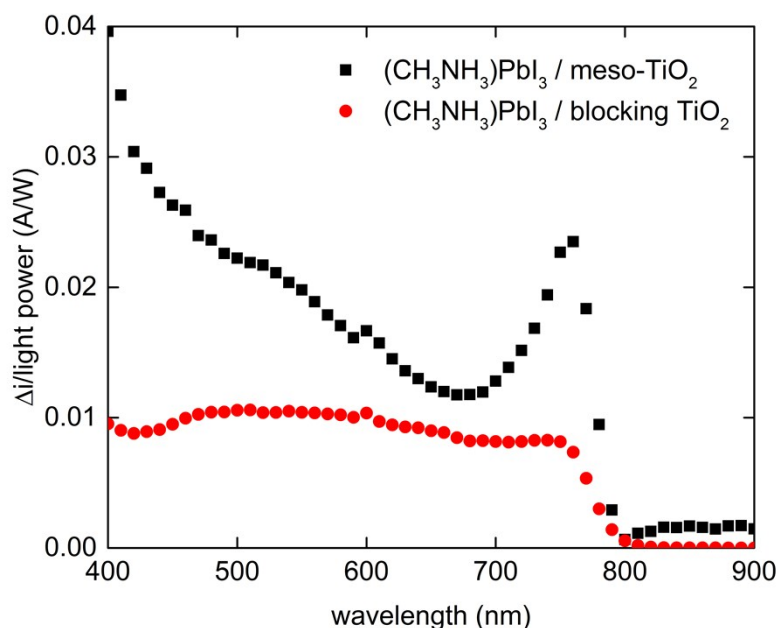


Fig. S2. The photocurrent of two devices, one consisting of $(\text{CH}_3\text{NH}_3)\text{PbI}_3$ in a mesoporous TiO_2 matrix (described further in main text) and one containing a dense, compact TiO_2 layer, a planar $(\text{CH}_3\text{NH}_3)\text{PbI}_3$ layer, and a PEDOT:PSS hole transport layer.

References:

1. Argazzi, R.; Bignozzi, C. A.; Heimer, T. A.; Castellano, F. N.; Meyer, G. J. *Inorg. Chem.* **1994**, *33*, 5741.

2. J. Burschka, N. Pellet, S.-J. Moon, R. Humphrey-Baker, P. Gao, M. K. Nazeeruddin, and M. Grätzel, *Nature*, 2013, **499**, 316.

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