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A 2-terminal perovskite/silicon multijunction solar cell enabled by a silicon tunnel junction

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With the advent of efficient high-bandgap metal-halide perovskite photovoltaics, an opportunity exists to make perovskite/silicon tandem solar cells. We fabricate a monolithic tandem by developing a silicon-based interband tunnel junction that facilitates majority-carrier charge recombination between the perovskite and silicon sub-cells. We demonstrate a 1 cm^2 2-terminal monolithic perovskite/silicon multijunction solar cell with a V_{OC} as high as 1.65 V. We achieve a stable 13.7% power conversion efficiency with the perovskite as the current-limiting sub-cell, and identify key challenges for this device architecture to reach efficiencies over 25%. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4914179>]

Solar-to-electricity conversion efficiency is the technical variable that most strongly influences silicon (Si) photovoltaic (PV) module costs.^{1,2} The record efficiency of crystalline silicon (c-Si) single-junction PV devices has increased from 25% to 25.6% during the last fifteen years,^{3,4} asymptotically approaching the 29.4% Auger-recombination-constrained Shockley-Queisser limit.⁵ To make PV modules with higher efficiency than market-leading c-Si while leveraging existing c-Si manufacturing capacity, Si-based tandem approaches have been proposed.^{6–10} The top sub-cell in a silicon-based tandem should have a band gap between 1.6 and 1.9 eV.¹¹ However, very few materials exhibit high open-circuit voltages (V_{OC}) within this band gap range. Recently, the methylammonium-lead-halide perovskite has demonstrated a rapid efficiency increase^{12–16} with a V_{OC} of 1.15 V.¹⁷ The methylammonium-lead-halide perovskite has a tunable band gap, ranging from 1.6 to 2.3 eV depending on halide composition,¹⁸ though not all compositions are currently stable under illumination.¹⁹ Methods to optically transmit longer-wavelength light through a top perovskite sub-cell in a mechanically stacked tandem configuration have been developed recently.^{9,20}

A perovskite/Si multijunction solar cell may also be constructed *via* monolithic integration where a thin film perovskite sub-cell is deposited directly onto the c-Si sub-cell. Monolithic integration requires electrical coupling between sub-cells and transmission of infrared light to the bottom sub-cell. We use an interband tunnel junction²¹ to facilitate electron tunneling from the electron-selective contact of the perovskite sub-cell into the *p*-type emitter of the Si sub-cell. This approach stands in contrast to the recombination layer used in other perovskite tandem systems²² and is the one widely used in III-V²³ and micromorph (*a*-Si/ μ c-Si)²⁴ tandem solar cells. Unlike the tunnel junction in III-V multijunction solar cells, our tunnel junction is made of silicon with an indirect band gap, enabling electrical coupling

with minimal parasitic absorption. The conduction-band alignment between Si and the perovskite sub-cell's electron-selective contact (TiO_2) enables bypassing the usage of a transparent conducting oxide (TCO) recombination layer, an alternative option with greater parasitic absorption. In this work, we use the methylammonium-lead(II)-iodide perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$), which has a 1.61 eV band gap.²⁵ Herein, we present the device design, fabrication, characterization, and loss analysis of monolithic perovskite/Si multijunction solar cells.

We develop a 2-terminal perovskite/Si multijunction architecture on an *n*-type Si solar cell (Figure 1(a)) with 1 cm^2

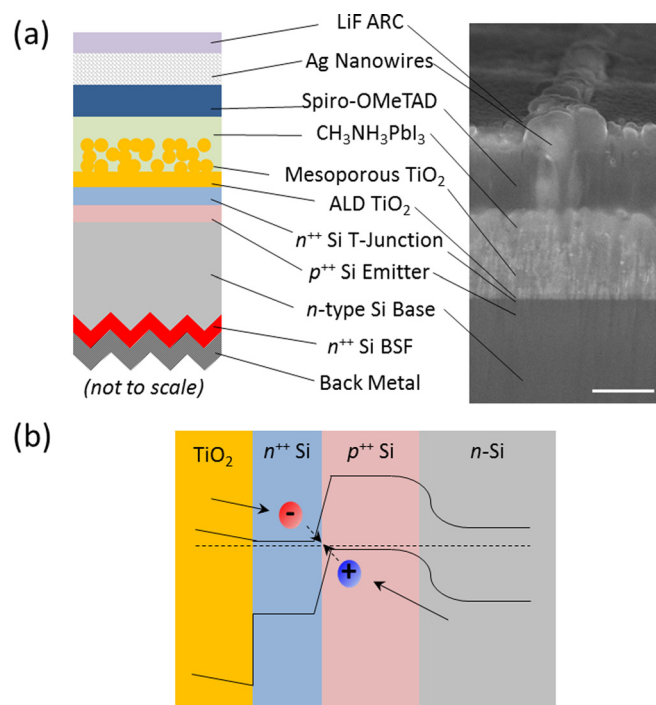


FIG. 1. (a) The device structure of a 2-terminal monolithically grown perovskite/Si multijunction solar cell with an *n*-type Si base. The polished SEM image is taken at 45° tilt to show the Ag nanowire mesh (500 nm scale bar). (b) Band diagram of the perovskite/silicon cell interface showing the charge-transport mechanism around the Si tunnel junction.

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area. We process an n -type Si sub-cell with planar top surface and full-area p -type emitter and n -type back surface field (BSF) using standard Si processing techniques.²⁶ A tunnel junction facilitates carrier recombination (holes from the n -type Si base passing through the p -type emitter and electrons from the perovskite layer passing through its TiO₂ electron transport layer, respectively, as shown in Figure 1(b)). We form an n^{++}/p^{++} tunnel junction by depositing heavily doped n^{++} hydrogenated amorphous silicon (a-Si:H) using plasma-enhanced chemical vapor deposition (PECVD).²⁶ The 30 nm-thick a-Si:H layer is subsequently annealed in N₂ ambient at 680 °C for 15 min to activate the dopants.²⁷ It is known that interdiffusion of dopant species during the device fabrication process (such as the dopant activation anneal) may degrade the tunnel junction conductivity. Accordingly, a 2–3 nm-thick intrinsic a-Si layer is inserted between the p^{++} emitter and the n^{++} amorphous Si layer during the PECVD process²⁶ to mitigate possible dopant interdiffusion.²⁸ After the dopant-activation anneal, the amorphous layers are partially crystallized as shown by transmission electron microscopy (TEM, Figure 2(a)). Using secondary ion mass spectrometry (SIMS), we show the dopant concentration on the n^{++}/p^{++} Si interface after the dopant activation anneal is 10^{19} – 10^{20} cm⁻³, which is suitable to form a high-quality inter-band tunnel junction (Figure 2(b)).²⁸

The addition of the tunnel junction on top of the single-junction n -type solar cell slightly reduces the short-circuit current (J_{SC}), but the presence of the tunnel junction has a

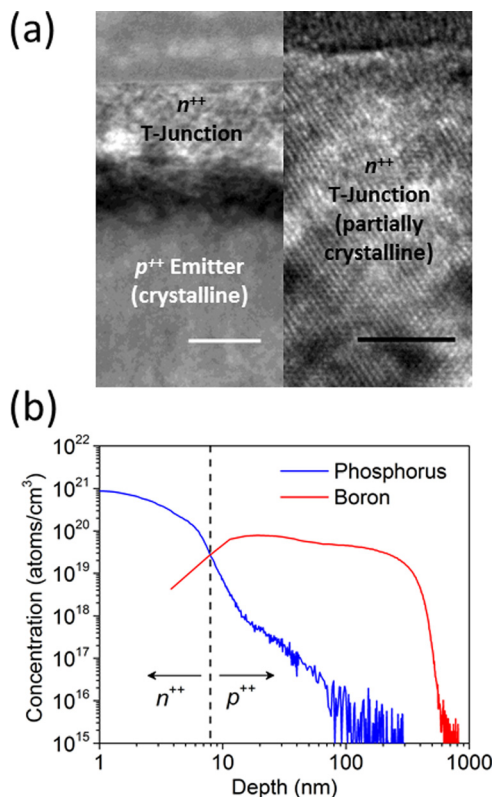


FIG. 2. (a) TEM image of the n^{++}/p^{++} silicon tunnel junction interface after the dopant activation annealing (left: 30 nm scale bar) and high-resolution TEM image of the n^{++} layer, showing the partially crystalline nature of this layer (right: 5 nm scale bar). (b) SIMS profile of the Si emitter and tunnel junction layer showing the sharp doping profile at the tunnel junction interface.

negligible effect on the series resistance (Figure S1) indicating proper operation of the tunnel junction.²⁶ The slight reduction in J_{SC} is due to parasitic absorption at $\lambda < 500$ nm (Figure S2),²⁶ which does not affect tandem performance as this portion of the spectrum is absorbed in the perovskite cell before reaching the tunnel junction.

The efficiency of the planar single-junction Si cells is 13.8%. This efficiency is lower than commercial averages in part due to tandem design considerations. These intentional design considerations are: (1) No surface texturing for light trapping is applied because a planar front surface simplifies deposition of the perovskite; (2) No p -type front surface passivation scheme is applied on the emitter because the same technique cannot be implemented on the n -type portion of the tunnel junction. Other causes of lower efficiency are: (1) full-area BSF passivation only provides moderate passivation; (2) a front surface passivation scheme that can be decoupled from the tunnel junction formation needs to be developed; (3) dedicated clean furnaces for emitter formation and back surface passivation are necessary to make more efficient Si sub-cells.

We fabricate the monolithic perovskite/Si multijunction solar cell by depositing a perovskite sub-cell on top of the tunnel junction. We first metallize the back of our Si sub-cell, then deposit a 30 nm-thick TiO₂ layer on the planar n^{++} c-Si front surface using atomic layer deposition (ALD).²⁶ This TiO₂ layer is the n -type heterojunction for the perovskite sub-cell. It is known that TiO₂ is a good electron-selective contact for c-Si because of its conduction-band alignment,²⁹ which also eases electron transport from the TiO₂ layer into the n^{++} Si tunnel junction layer.^{30,31} The thickness of this ALD TiO₂ layer can impact the optical transmission into the Si sub-cell (Figure S3),²⁶ and hence further thickness optimization is needed. The perovskite is deposited onto a mesoporous TiO₂ layer in a two-step conversion method.^{15,26} An organic p -type heterojunction contact, spiro-OMeTAD, is deposited by spin-coating on top of the perovskite and is chemically doped with spiro-(TSFI)₂.³² The top silver nanowire (AgNW) electrode is deposited using the procedure developed by Bailie *et al.*⁹ AgNWs are sprayed from solution onto a plastic (PET) film, and then transferred from the PET to the spiro-OMeTAD layer via mechanical transfer through the application of pressure via a ball bearing. The silver nanowire electrode before transfer has a sheet resistance of 9 Ω/\square with a peak transmission of 89.5%. A 111-nm-thick lithium fluoride (LiF) anti-reflection layer is then deposited by thermal evaporation.

The J - V curve of our 2-terminal perovskite/Si multijunction solar cell under simulated AM1.5G illumination is shown in Figure 3(a). Due to the hysteresis often observed in metal-halide perovskite solar cells, it is important to be rigorous with J - V characterization.³³ We use a 5 s delay after each 100 mV voltage step before measuring the current in both scan directions. However, we still find hysteresis at this scan rate and that up to 30 s is required to reach a steady-state. This yields an overestimation of the efficiency when scanning from forward to reverse bias and an underestimation when scanning from reverse to forward bias.³³ We measure the steady-state values of the three critical points on the J - V curve: open circuit (V_{OC}), short circuit (J_{SC}), and the

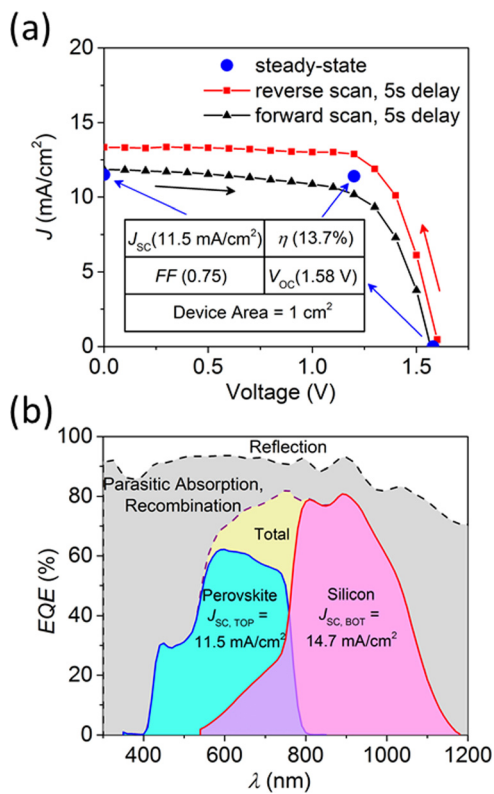


FIG. 3. (a) J - V curve of the 2-terminal perovskite/silicon multijunction solar cell under AM1.5G illumination. Forward and reverse-bias scan directions are shown with 5 s measurement delay per data point. Steady-state values for J_{SC} , V_{OC} , and MPP are measured by averaging over 30 s after reaching steady state. (b) Total device reflection and EQE of the perovskite and Si sub-cells of a typical perovskite/Si multijunction cell. The perovskite sub-cell EQE is corrected to match the measured J_{SC} and the silicon sub-cell EQE is reported as measured.²⁶

maximum power point (MPP), depicted as blue circles (color online) in Figure 3(a) to negate hysteretic effects. The steady-state J_{SC} is 11.5 mA/cm², the steady-state V_{OC} is 1.58 V, and the steady-state MPP is 13.7% at 1.20 V bias (Figure S4).²⁶ These resultant fill factor (FF) is 0.75. The 1 cm² cell was aperture-masked to ensure a correct illumination area. The V_{OC} has been measured as high as 1.65 V in some devices. This result is encouraging, as the V_{OC} is approximately the sum of the V_{OC} for the perovskite top sub-cell and the bottom Si sub-cell illuminated through a separate semi-transparent perovskite device on FTO⁹ (approximately 1.05 V and 0.55 V, respectively), further indicating proper operation of the tunnel junction.

The slow current-dynamics and corresponding hysteresis observed in the tandem resemble the sluggish dynamics of our perovskite solar cells and suggest that the perovskite sub-cell limits the current of the tandem.³³ This finding is substantiated by external quantum efficiency (EQE) measurements (Figure 3(b)) of the individual sub-cells.²⁶ Our tandem J_{SC} of 11.5 mA/cm² is low because the perovskite is illuminated through the p -type heterojunction, opposite from conventional perovskite devices. To understand the directional dependence of illumination on the perovskite sub-cell, we illuminate a semi-transparent single-junction perovskite solar cell⁹ through the TiO₂ heterojunction and through the spiro-OMeTAD heterojunction. When illuminated through

the TiO₂ heterojunction, the EQE of the semi-transparent cell integrates to 17.3 mA/cm², whereas when illuminated through the spiro-OMeTAD heterojunction the EQE integrates to 11.4 mA/cm² (Figure S5) due to low EQE for $\lambda < 550$ nm.²⁶ We attribute the lower photocurrent from the spiro-OMeTAD-side to parasitic absorption by the doped spiro-OMeTAD layer. From absorption measurements of doped spiro-OMeTAD on glass (Figure S6),²⁶ we estimate that the absorbed flux of the AM1.5G spectrum in this layer is 6.4 mA/cm² from 300–750 nm. We find that parasitic absorption by spiro-OMeTAD also reduces the photocurrent available to the bottom Si sub-cell, absorbing the equivalent of 2.0 mA/cm² of infrared photons from 750–1200 nm. The parasitic absorption can be reduced with a thinner spiro-OMeTAD layer, which is currently optimized to planarize a rough perovskite top surface to enable deposition of the silver nanowire electrode. With smoother perovskite films, the spiro-OMeTAD layer can achieve planarization with a thinner layer. The parasitic absorption may be completely removed by replacement of spiro-OMeTAD with an alternate p -type heterojunction contact that simultaneously exhibits both good conductivity and low parasitic absorption.

The perovskite sub-cell is also limited by quality of the perovskite absorber. Our single-junction perovskite cells with gold back contacts fabricated as control devices achieve at best 13.5% efficiency. Optimization of deposition conditions, precursor materials, and annealing protocols along with replacement or reduction of the spiro-OMeTAD layer is expected to yield a perovskite top sub-cell equivalent to the record single-junction perovskite cell, which currently stands at 20.1%.³ For the Si sub-cell, applying a back-surface field and excellent surface passivation to the back of the bottom Si sub-cell, using dedicated furnaces, and decoupling the front surface passivation scheme from the tunnel junction formation are expected to yield improvements. We predict a Si sub-cell with a V_{OC} of 660–720 mV and a matched tandem J_{SC} of 18–19 mA/cm² when illuminated through the perovskite sub-cell. We expect, with these changes designed to improve the sub-cells to the match the highest quality devices available today, the monolithic tandem would have a V_{OC} of 1.84 V, a J_{SC} of 19 mA/cm², a FF of 0.83, and a corresponding efficiency of 29.0%. Ultimately, it has been suggested that perovskite/Si monolithic tandems can surpass 35% efficiency through careful photon management.¹⁰

In summary, we have demonstrated a 1 cm², 2-terminal monolithically-integrated metal-halide perovskite/Si multijunction solar cell. The monolithic integration is enabled by a Si-based tunnel junction fabricated directly on top of the bottom Si sub-cell emitter and by incorporating a semi-transparent silver nanowire-based top electrode. We obtained a multijunction device V_{OC} as high as 1.65 V, which is the expected sum of the perovskite and filtered Si V_{OC} 's, demonstrating the potential of this approach. The best 2-terminal multijunction prototype device efficiency is 13.7% and is current-limited by the perovskite sub-cell. This value is low compared to the record efficiency for perovskite or Si cells, in part because this tandem prototype does not yet have best-in-class perovskite and Si layers. Further improvements can be achieved by replacing the spiro-OMeTAD layer with wider band gap hole transport material, improving the

quality of the perovskite absorber, use of dedicated furnaces for the Si sub-cell fabrication, and by implementing better surface passivation schemes on the front and back side of the Si sub-cell. These improvements can yield a 29.0% efficient tandem, with the ultimate efficiency potential of these monolithic tandems surpassing 35%.

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¹P. A. Basore, *IEEE J. Photovoltaics* **4**, 1477 (2014).

²D. M. Powell, M. T. Winkler, A. Goodrich, and T. Buonassisi, *IEEE J. Photovoltaics* **3**, 662 (2013).

³M. A. Green, K. Emery, Y. Hishikawa, W. Warta, and E. D. Dunlop, *Prog. Photovoltaics Res. Appl.* **23**, 1 (2015).

⁴K. Masuko, M. Shigematsu, T. Hashiguchi, D. Fujishima, M. Kai, N. Yoshimura, T. Yamaguchi, Y. Ichihashi, T. Mishima, N. Matsubara, T. Yamanishi, T. Takahama, M. Taguchi, E. Maruyama, and S. Okamoto, *IEEE J. Photovoltaics* **4**, 1433 (2014).

⁵R. M. Swanson, in Proceedings of 31st IEEE Photovoltaic Specialist Conference (2005), Vol. 889.

⁶M. Umeno, T. Soga, K. Baskar, and T. Jimbo, *Sol. Energy Mater. Sol. Cells* **50**, 203 (1998).

⁷K. Tanabe, K. Watanabe, and Y. Arakawa, *Sci. Rep.* **2**, 349 (2012).

⁸Z. M. Beiley and M. D. McGehee, *Energy Environ. Sci.* **5**, 9173 (2012).

⁹C. D. Bailie, M. G. Christoforo, J. P. Mailoa, A. R. Bowring, E. L. Unger, W. H. Nguyen, J. Burschka, N. Pellet, J. Z. Lee, M. Grätzel, R. Noufi, T. Buonassisi, A. Salleo, and M. D. McGehee, *Energy Environ. Sci.* **8**, 956 (2015).

¹⁰P. Loper, B. Niesen, S.-J. Moon, S. Martin de Nicolas, J. Holovsky, Z. Remes, M. Ledinsky, F.-J. Haug, J.-H. Yum, S. De Wolf, and C. Ballif, *IEEE J. Photovoltaics* **4**, 1545 (2014).

¹¹F. Meillaud, A. Shah, C. Droz, E. Vallat-Sauvain, and C. Miazza, *Sol. Energy Mater. Sol. Cells* **90**, 2952 (2006).

¹²M. Liu, M. B. Johnston, and H. J. Snaith, *Nature* **501**, 395 (2013).

¹³M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami, and H. J. Snaith, *Science* **338**, 643 (2012).

¹⁴J.-H. Im, C.-R. Lee, J.-W. Lee, S.-W. Park, and N.-G. Park, *Nanoscale* **3**, 4088 (2011).

¹⁵J. Burschka, N. Pellet, S.-J. Moon, R. Humphry-Baker, P. Gao, M. K. Nazeeruddin, and M. Grätzel, *Nature* **499**, 316 (2013).

¹⁶N. J. Jeon, J. H. Noh, W. S. Yang, Y. C. Kim, S. Ryu, J. Seo, and S. Il Seok, *Nature* **517**, 476 (2015).

¹⁷A. Ishii, A. K. Jena, and T. Miyasaka, *APL Mater.* **2**, 091102 (2014).

¹⁸J. H. Noh, S. H. Im, J. H. Heo, T. N. Mandal, and S. Il Seok, *Nano Lett.* **13**, 1764 (2013).

¹⁹E. T. Hoke, D. J. Slotcavage, E. R. Dohner, A. R. Bowring, H. I. Karunadasa, and M. D. McGehee, *Chem. Sci.* **6**, 613 (2015).

²⁰P. Löper, S.-J. Moon, S. Martin de Nicolas, B. Niesen, M. Ledinsky, S. Nicolay, J. Bailat, J.-H. Yum, S. De Wolf, and C. Ballif, *Phys. Chem. Chem. Phys.* **17**, 1619 (2015).

²¹L. Esaki, *Phys. Rev.* **109**, 603 (1958).

²²T. Todorov, T. Gershon, O. Gunawan, C. Sturdevant, and S. Guha, *Appl. Phys. Lett.* **105**, 173902 (2014).

²³G. J. Bauhuis, P. Mulder, and J. J. Schermer, *Prog. Photovoltaics Res. Appl.* **22**, 656 (2014).

²⁴F. A. Rubinelli, J. K. Rath, and R. E. I. Schropp, *J. Appl. Phys.* **89**, 4010 (2001).

²⁵K. Tvingstedt, O. Malinkiewicz, A. Baumann, C. Deibel, H. J. Snaith, V. Dyakonov, and H. J. Bolink, *Sci. Rep.* **4**, 6071 (2014).

²⁶See Supplementary Material at <http://dx.doi.org/10.1063/1.4914179> for fabrication and characterization details.

²⁷Y. Wang, X. Liao, Z. Ma, G. Yue, H. Diao, J. He, G. Kong, Y. Zhao, Z. Li, and F. Yun, *Appl. Surf. Sci.* **135**, 205 (1998).

²⁸N. Jin, S. Chung, A. T. Rice, P. R. Berger, P. E. Thompson, C. Rivas, R. Lake, S. Sudirgo, J. J. Kempisty, B. Curanovic, S. L. Rommel, K. D. Hirschman, S. K. Kurinec, P. H. Chi, and D. S. Simons, *IEEE Trans. Electron Devices* **50**, 1876 (2003).

²⁹D. Gebeyehu, C. J. Brabec, N. S. Sariciftci, D. Vangeneugden, and R. Kiebooms, *Synth. Met.* **125**, 279 (2001).

³⁰S. Avasthi, W. E. McClain, G. Man, A. Kahn, J. Schwartz, and J. C. Sturm, *Appl. Phys. Lett.* **102**, 203901 (2013).

³¹J. Jhaveri, S. Avasthi, K. Nagamatsu, and J. C. Sturm, in Proceedings of 40th IEEE Photovoltaic Specialist Conference (2014), Vol. 1525.

³²W. H. Nguyen, C. D. Bailie, E. L. Unger, and M. D. McGehee, *J. Am. Chem. Soc.* **136**, 10996 (2014).

³³E. L. Unger, E. T. Hoke, C. D. Bailie, W. H. Nguyen, A. R. Bowring, T. Heumüller, M. G. Christoforo, and M. D. McGehee, *Energy Environ. Sci.* **7**, 3690 (2014).