

Organometal Halide Perovskites for Transformative Photovoltaics

rganometal halide perovskite-based solar cells have recently emerged as a transformative photovoltaic (PV) technology. Two important journals, Science (DOI: 10.1126/ science.342.6165.1438-b) and Nature (http://www.nature. com/news/365-days-nature-s-10-1.14367), both highlighted perovskite photovoltaics as one of the major scientific breakthroughs of the year 2013. Power conversion efficiency attained with the hybrid organic-inorganic perovskite CH₃NH₃PbI₃ has now exceeded 15%, making it competitive with thin-film PV technology. Decades-long basic research on dye-sensitized solar cells and quantum dot solar cells has now led to the development of perovskite PVs.¹ The most attractive aspects of this technology are the simplicity of photoactive layer synthesis and application using benchtop approaches at temperatures less than 100 °C. A renewed enthusiasm has arisen among scientists in the field to continue developing economically viable next-generation PV technology. Recently, Perspective articles that highlight the evolution of perovskite PVs have identified areas of future growth for achieving efficiencies surpassing 20%.^{2,3} In this ACS Selects issue we present selected recent articles that focus on new methods and physical insights into the operation of organometal halide perovskite solar cells.

Following the discovery of these organometal halide materials by Mitzi's group in the 1990s,⁴ Miyasaka's group uncovered their photoelectrochemical properties in 2009.⁵ Because of the instability of CH₃NH₃PbI₃ in a solvent medium, research on this material remained dormant until solid-state solar cells were designed in 2012.^{6,7} The first attempt was by the Kanatzidis group using CsSnI₃ as a solid hole conductor in dye-sensitized solar cells,⁶ followed by Grätzel and co-workers utilizing CH₃NH₃PbI₃ as a light absorber.⁷ The CH₃NH₃PbI₃ absorber can be easily prepared by dissolving equimolar amounts of methylammonium iodide (CH₃NH₃I) and lead(II) iodide (PbI₂) solutions in anhydrous γ -butyrolactone at 70 °C. This solution, when spin-cast onto a mesoscopic titanium dioxide (TiO_2) or aluminum oxide (Al_2O_3) film followed by drying at 70-80 °C, forms dark-colored crystalline CH₃NH₃PbI₃ film with absorptions up to 800 nm (bandgap 1.5 eV). Some variations in synthesis include planar films without the mesoscopic templates, sequential exposure, and vapor-phase exposure of reactants.^{3,8} X-ray diffraction and Raman techniques have proven to be useful tools for characterizing the perovskite structure.9 The electronic structure and occupied energy levels of CH₃NH₃PbI₃ deposited onto mesoporous TiO₂ have been determined using photoelectron spectroscopy with hard X-rays.¹⁰

An important and useful feature of these organometal halide perovskite solar cells is the relatively high open-circuit voltage $(V_{\rm OC} \approx 1 \text{ V})$. New strategies are now being explored to boost the open-circuit voltage even higher using CH₃NH₃PbBr₃.^{11,12} For example, inclusion of chloride ions in CH₃NH₃PbBr₃ films yields $V_{\rm OC}$ as high as 1.5 V. Density functional theory is being applied to establish the semiconducting properties and find ways to manipulate band structure energetics.¹³⁻¹⁵ Recent efforts focus on identifying ambipolar charge-transport properties and the importance of spin—orbit coupling in organometal halide perovskites.^{14,15} In addition, a vapor-assisted solution process to construct polycrystalline perovskite thin films as well as nanometer-sized CH₃NH₃PbBr₃ nanoparticles is facilitating new ways to probe the excited-state and charge-transport properties of this novel class of materials.^{8,16}

The charge-separation, charge-recombination, and chargetransport properties of the organometal halide perovskite films coated on mesoscopic oxide films differ from those of other thin-film semiconductor PVs.^{2,3,17,18} To date, most of the reported studies employ spiro-OMeTAD as the hole conductor. Research is underway to explore alternate organic and inorganic hole conductors.^{19–22} Higher hole conductivity reported for inorganic hole conductors has been shown to be possible using cheaper and readily available materials such as CuI.²¹ A basic understanding of the hole transport properties is crucial for further development of perovskite solar cells.

The papers presented in this ACS Selects collection focus on the physical chemistry aspects of the newly emerging field of organometal halide perovskites and provide key insights into their structural, optical, and charge-transport properties.

Prashant V. Kamat, Deputy Editor

Journal of Physical Chemistry Letters

AUTHOR INFORMATION

Notes

Views expressed in this Editorial are those of the author and not necessarily the views of the ACS.

RELATED READINGS

(1) Bisquert, J. The Swift Surge of Perovskite Photovoltaics. J. Phys. Chem. Lett. 2013, 4, 2597–2598.

(2) Park, N. G. Organometal Perovskite Light Absorbers Toward a 20% Efficiency Low-Cost Solid-State Mesoscopic Solar Cell. J. Phys. Chem. Lett. 2013, 424232429

(3) Snaith, H. J. Perovskites: The Emergence of a New Era for Low-Cost, High-Efficiency Solar Cells. J. Phys. Chem. Lett. **2013**, *4*, 3623–3630.

(4) Wang, S.; Mitzi, D. B.; Feild, C. A.; Guloy, A. Synthesis and Characterization of $[NH_2C(I):NH_2]_3MI_5$ (M = Sn, Pb): Stereochemical Activity in Divalent Tin and Lead Halides Containing Single (110) Perovskite Sheets. *J. Am. Chem. Soc.* **1995**, *117*, 5297–5302.

(5) Kojima,A.; Teshima, K.; Shirai, Y.; Miyasaka, T. Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells. J. Am. Chem. Soc. 2009, 131, 6050–6051.

(6) Chung, I.; Lee, B.; He, J. Q.; Chang, R. P. H.; Kanatzidis, M. G. All-Solid-State Dye-Sensitized Solar Cells with High Efficiency. *Nature* **2012**, *485*, 486–494.

(7) Etgar, L.; Gao, P.; Xue, Z.; Peng, Q.; Chandiran, A. K.; Liu, B.; Nazeeruddin, Md. K.; Grätzel, M. Mesoscopic $CH_3NH_3PbI_3/TiO_2$ Heterojunction Solar Cells. *J. Am. Chem. Soc.* **2012**, *134*, 17396–17399.

(8) Chen, Q.; Zhou, H.; Hong, Z.; Luo, S.; Duan, H.-S.; Wang, H.-H.; Liu, Y.; Li, G.; Yang, Y.; Planar Heterojunction Perovskite Solar

Published: March 12, 2014

Cells via Vapor Assisted Solution Process. J. Am. Chem. Soc. 2014, 136, 622–625.

(9) Quarti, C.; Grancini, G.; Mosconi, E.; Bruno, P.; Ball, J. M.; Lee, M. M.; Snaith, H. J.; Petrozza, A.; De Angelis, F. The Raman Spectrum of the CH₃NH₃PbI₃ Hybrid Perovskite: Interplay of Theory and Experiment. *J. Phys. Chem. Lett.* **2014**, *5*, 279–284.

(10) Lindblad, R.; Bi, D.; Park, B.-W.; Oscarsson, J.; Gorgoi, M.; Siegbahn, H.; Odelius, M.; Johansson, E. M. J.; Rensmo, H. The Electronic Structure of $TiO_2/CH_3NH_3PbI_3$ Perovskite Solar Cell Interfaces. J. Phys. Chem. Lett. **2014**, 5, 648–653.

(11) Edri, E.; Kirmayer, S.; Cahen, D.; Hodes, G. High Open-Circuit Voltage Solar Cells Based on Organic-Inorganic Lead Bromide Perovskite. J. Phys. Chem. Lett. **2013**, *4*, 897–902.

(12) Edri, E.; Kirmayer, S.; Kulbak, M.; Hodes, G.; Cahen, D. Chloride Inclusion and Hole Transport Material Doping to Improve Methyl Ammonium Lead Bromide Perovskite-Based High Open-Circuit Voltage Solar Cells. J. Phys. Chem. Lett. **2014**, *5*, 429–433.

(13) Giorgi, G.; Fujisawa, J.-I.; Segawa, H.; Yamashita, K. Small Photocarrier Effective Masses Featuring Ambipolar Transport in Methylammonium Lead Iodide Perovskite: A Density Functional Analysis. J. Phys. Chem. Lett. **2013**, *4*, 4213–4216.

(14) Mosconi, E.; Amat, A.; Nazeeruddin, M. K.; Grätzel, M.; De Angelis, F. First-Principles Modeling of Mixed Halide Organometal Perovskites for Photovoltaic Applications. *J. Phys. Chem. C* 2013, *117*, 13902–13913.

(15) Even,J.; Pedesseau, L.; Jancu, J.-M.; Katan, C. Importance of Spin–Orbit Coupling in Hybrid Organic/Inorganic Perovskites for Photovoltaic Applications. J. Phys. Chem. Lett. **2013**, *4*, 2999–3005.

(16) Schmidt,L. C.; Pertegás, A.; González-Carrero, S.; Malinkiewicz, O.; Agouram, S.; Mínguez Espallargas, G.; Bolink, H. J.; Galian, R. E.; Pérez-Prieto, J. Nontemplate Synthesis of CH₃NH₃PbBr₃ Perovskite Nanoparticles. J. Am. Chem. Soc. **2014**, *136*, 850–853.

(17) Zhao, Y.-X.; Zhu, K. Charge Transport and Recombination in Perovskite (CH₃NH₃)PbI₃ Sensitized TiO₂ Solar Cells. *J. Phys. Chem. Lett.* **2013**, *4*, 2880–2884.

(18) Zhao, Y.; Nardes, A. M.; Zhu, K. Solid-State Mesostructured Perovskite CH₃NH₃PbI₃ Solar Cells: Charge Transport, Recombination, and Diffusion Length. *J. Phys. Chem. Lett.* **2014**, *5*, 490–494.

(19) Koh, T. M.; Fu, K.; Fang, Y.; Chen, S.; Sum, T. C.; Mathews, N.; Mhaisalkar, S. G.; Boix, P. P.; Baikie, T. Formamidinium-Containing Metal-Halide: An Alternative Material for Near-IR Absorption Perovskite Solar Cells. *J. Phys. Chem. C* **2014**, *118*, ASAP (DOI: 10.1021/jp411112k).

(20) Bi, D.-Q.; Yang, L.; Boschloo, G.; Hagfeldt, A.; Johansson, E. M. J. Effect of Different Hole Transport Materials on Recombination in CH₃NH₃PbI₃ Perovskite-Sensitized Mesoscopic Solar Cells. *J. Phys. Chem. Lett.* **2013**, *4*, 1532–1536.

(21) Christians, J. A.; Fung, R. C. M.; Kamat, P. V. An Inorganic Hole Conductor for Organo-Lead Halide Perovskite Solar Cells. Improved Hole Conductivity with Copper Iodide. *J. Am. Chem. Soc.* **2014**, *136*, 758–764.

(22) Jeon, N. J.; Lee, J.; Noh, J. H.; Nazeeruddin, M. K.; Grätzel, M.; Seok, S. I. Efficient Inorganic–Organic Hybrid Perovskite Solar Cells Based on Pyrene Arylamine Derivatives as Hole-Transporting Materials. J. Am. Chem. Soc. **2013**, 135, 19087–19090.