

QUANTUM DOT PHOTOVOLTAICS

Getting high with quantum dot solar cells

Colloidal perovskite quantum dots offer potential stability advantages for solar cells over bulk perovskites but lag far behind in device efficiency. Now, a modified cation exchange method has been shown to improve the optoelectronic quality of perovskite nanocrystals, improving further the efficiency and stability of quantum dot solar cells.

Joel Jean

Among emerging solar technologies, perovskite solar cells have so far come closest to the ideal of high efficiency, low cost and simple manufacturability. Most major photovoltaic (PV) manufacturers and a bevy of start-ups are investigating perovskites as a near-term complement and potential long-term successor to crystalline silicon. However, long-term device stability remains an open question: it is not yet clear how to engineer perovskites to reach the 25-year lifetime typically expected of commercial PV modules.

One potential strategy to tackle stability is to reduce the perovskite dimensionality. Both layered two-dimensional (2D) films and nanocrystal quantum dots (QDs) have shown promise for more stable solar cells than conventional 3D perovskite films. In addition, wide-bandgap perovskite QDs have shown increased phase stability, compositional tunability, and open-circuit voltages compared to perovskite thin films with similar compositions, potentially making them an ideal absorber for the top cell in tandems with perovskites, silicon or copper indium gallium selenide (CIGS). But QDs lag far behind thin films in power conversion efficiency, with a previous certified cell record of 13.4% for QDs¹ compared to 25.2% for thin films². Writing in *Nature Energy*, Mengmeng Hao and colleagues from Australia, China and the UK report a significant improvement in the efficiency of QD devices, up to a certified value of 16.6%, enabled by improving the synthesis of high-quality multi-cation perovskite QDs³.

Hao and co-workers use a modified cation exchange method to synthesize high quality $\text{Cs}_{1-x}\text{FA}_x\text{PbI}_3$ QDs (where FA is formamidinium) with a wide range of compositions ($x = 0-1$). The same QD compositions had previously been synthesized with cation exchange but did not produce more efficient solar cells than single-cation CsPbI_3 QDs, likely because short carrier lifetimes and diffusion lengths

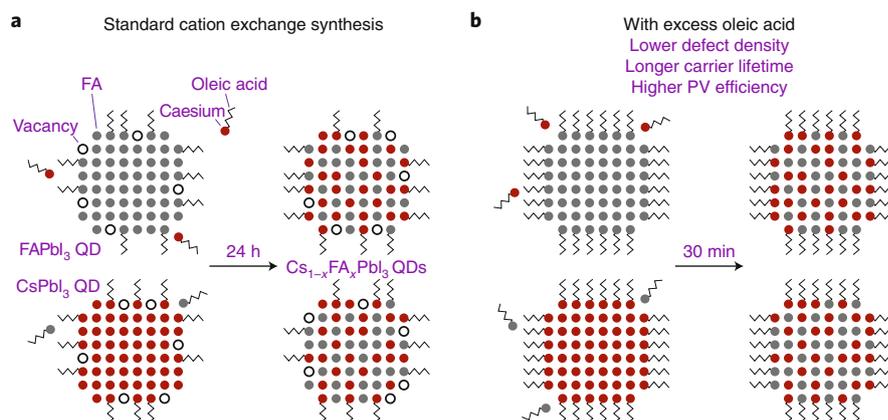


Fig. 1 | QD synthesis by ligand-assisted cation exchange. **a**, Schematic of the standard cation exchange process for synthesizing mixed-cation perovskite QDs. Cation mixing is slow and cation vacancies are present after the synthesis. **b**, Modified synthesis process with excess oleic acid. The oleic acid ligands promote the solvation, diffusion and cross-exchange of cations, producing QDs with improved optoelectronic properties and device performance.

limited the efficiency of charge extraction^{4,5}. Following these previous reports, the researchers mix CsPbI_3 and FAPbI_3 QDs and monitor the exchange of Cs and FA cations between the parent QDs. Unlike previous work, however, they intentionally increase the concentration of oleic acid ligands in the solution — these ligands help solvate the cations, stimulating the formation and diffusion of A-site vacancies and expediting the exchange reaction (Fig. 1). This seemingly minor change has a major impact on the QD optoelectronic properties and solar cell performance.

The resulting $\text{Cs}_{1-x}\text{FA}_x\text{PbI}_3$ QD solar cells reach a higher short-circuit current and open-circuit voltage than those prepared without excess oleic acid. The researchers propose that without excess ligands, insufficient ligand coverage of the QD surfaces allows more defects to form during the cation exchange reaction. Their hypothesis is supported by experimental evidence — with the

oleic-acid-rich preparation^{4,5}, they observe increased photoluminescence lifetimes and reduced defect counts in high-resolution scanning tunnelling electron microscopy (STEM) images.

The ligand-assisted cation exchange technique allows Hao and co-workers to achieve a certified efficiency for QD solar cells of 16.6%. This represents a substantial step forward in QD PV efficiency. Importantly, these high-performance devices are also relatively stable, losing less than 10% of their initial efficiency after 600 hours under open-circuit conditions in inert atmosphere, compared to over 20% for bulk control devices with the same perovskite compositions.

Besides further improvements in efficiency and stability, substantial challenges to commercialization of QD solar cells remain. Two key challenges include developing high-throughput deposition methods and reducing materials cost. Commercial silicon PV modules today

routinely exceed 19% efficiency over square metre areas, with record cells surpassing 26% — the small-area single-junction perovskite QD cell record of 16.6% will likely need to break 20% to be commercially relevant for tandem applications, and even higher for single-junction applications. Cell and module stability must be proven over longer time periods and under practical operating conditions, with maximum power point tracking, variable temperature and different environmental conditions.

The current method used to deposit perovskite QD films — layer-by-layer spin-coating — involves alternating deposition and solvent treatment of thin (<100 nm) QD layers to remove long-chain surface ligands. This makes the QD film more electrically conductive and resistant to re-dissolution and allows a thick film to form. However, layer-by-layer deposition cannot easily scale to high volume production. A promising ink-based approach has been demonstrated for lead chalcogenide QDs^{7,8}, but has not yet been proven for perovskite QDs.

Finally, QD PV material costs remain too high. The device structure used by

Hao and colleagues employs expensive contact materials (for example, Spiro-OMeTAD and gold). Even more critically, the cost of synthesizing QDs is a major barrier — recent calculations suggest that the present perovskite QD synthesis cost per watt, even assuming an optimistic 20% cell efficiency that is likely needed to be commercially relevant, is more than the cost per watt of an entire silicon PV module⁹. The purification (crash out) step is particularly expensive, as it is labour intensive, has substantial yield loss and uses expensive solvents — Hao and colleagues use two crash out cycles, similar to previous reports. New low-cost, high-throughput synthetic methods are needed for perovskite QDs. Ultimately, to enter the PV market and achieve scale, QD solar cells may need to address niche, high-value applications where cost is not the only variable in the purchasing decision.

While the aspects above become relevant when thinking of industrial manufacturing, achieving a competitive power conversion efficiency is the cornerstone of any emerging PV commercialization strategy. The work

by Hao and colleagues takes a major step in this direction for perovskite QD solar cells, while also providing a foundation for the development of other high-performance QD optoelectronic devices. □

Joel Jean 

Swift Solar Inc., San Carlos, CA, USA.
e-mail: jjean@alum.mit.edu

Published online: 20 January 2020

<https://doi.org/10.1038/s41560-019-0534-8>

References

1. Sanehira, E. M. et al. *Sci. Adv.* **3**, eaao4204 (2017).
2. Yoo, J. J. et al. *Energy Environ. Sci.* **12**, 2192–2199 (2019).
3. Hao, M. et al. *Nat. Energy* <https://doi.org/10.1038/s41560-019-0535-7> (2020).
4. Protesescu, L. et al. *ACS Nano* **11**, 3119–3134 (2017).
5. Hazarika, A. et al. *ACS Nano* **12**, 10327–10337 (2018).
6. *Best Research-Cell Efficiencies* (National Renewable Energy Laboratory, 2019); <https://www.nrel.gov/pv/assets/pdfs/best-research-cell-efficiencies.20191106.pdf>
7. Fischer, A. et al. *Adv. Mater.* **25**, 5742–5749 (2013).
8. Aqoma, H. & Jang, S.-Y. *Energy Environ. Sci.* **11**, 1603–1609 (2018).
9. Jean, J. et al. *Energy Environ. Sci.* **11**, 2295–2305 (2018).

Competing interests

The author is a founder and chief executive officer of Swift Solar, a US company developing perovskite photovoltaics.