Quantum Dots and Perovskites – Realizing the Best of Both Worlds for Revolutionary Optoelectronic Applications

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1,156 kW

720 kW

524 kW

857 kW

94 kW

524 kW
• 2023 before the global cumulative capacity is at 1 TW
• At current rates, over 400 years to produce 30 TW
If we can “print” solar cells like we print newspaper, we could cheaply produce all the electricity we need very rapidly.

1 “upcycled” newspaper plant could produce a TW/yr

- Printable perovskites offer a revolutionary new PV technology
  - Perovskite stand alone devices
  - Perovskite / perovskite tandems
  - Perovskite / other technologies
Important new markets for PV

- Building integrated PV
  - Switchable windows
- Wearable PV
- Disaster Relief
- Mobile electricity
  - Self powered drone technologies
  - Car trickle chargers
- Power Beaming

Thin film (bulk) perovskites vs Nanocrystals

Solvated Perovskite precursor molecules which crystalize as the solvent dries

Perovskite nanocrystals in solution
Silicon – industry leader for utility/residential PV

Best Research-Cell Efficiencies

- Multi-junction cells (2-terminal, monolithic)
- LM = silicon-etched
- MM = micromorph
- Thin-film, metamorphic
- Thin-film, concentrator
- Two-junction (non-concentrator)
- Two-junction (nano-concentrator)
- Four-junction or more (non-concentrator)

Single-Junction GaAs
- Single crystal
- Concentrator
- Thin-film crystal

Crystalline Si Cells
- Single crystal (non-concentrator)
- Multicrystalline
- Silicon heterostructures (HT)
- Thin-film crystal

Efficiency (%) vs. Years (1975-2020)

NATIONAL RENEWABLE ENERGY LABORATORY
III-V semiconductors – highest efficiency & cost

Typically used in space applications where fabrication cost is less critical than deployment

$25,000 to lift a pound into space
Emerging PV offers potential – but still emerging

Best Research-Cell Efficiencies

Organic semiconductors, organic dyes, nanomaterials & Perovskites
Pb-halide Perovskite semiconductors

Perovskites: Efficient, inexpensive, flexible, radiation hard, tunable (composition, size)...

How did Pb-halide Perovskite PVs get to where they are?

• Incredible rise in efficiency (<4 to 23% short time)

• As tolerant to defects as any other electronic material we know.

• Solution or vapor-deposited material

• New Semiconductor system poised to greatly reform optoelectronics:
  o Solar Cells
  o LED / Solid State Lighting
  o TV / Display technology
  o Quantum Computation, spin devices/memory
  o Lasers, photodetectors, sensors, Gamma detectors

• Stability and Phase Transitions are critical to understand before deployment.
Perovskite stability

- Identify the unstable part of perovskite solar cells and fix it
  - Why is this so challenging?
    - Ion migration (Li, A-site cation, halides, metals)
    - Moisture ingress
    - Low formation energy for crystallization

Constant need for studies providing greater insight into degradation

As a function of:
- Atmosphere (temperature, humidity, ...)
- Device configuration (absorber chemistry, ETL, HTL, additives (Li+, etc.) & concentration, electrodes, polarity)
- Substrate

All while tracking output under standardized measurement conditions

**Perovskite Active Layer:** Phase segregation, phase stability, ion migration, thermal decomposition...

**Interfaces:** Band alignment, trapped charges, catalysis, water ingress...

**Contact Layers:** doping, redox, thermal stability...
Where are the weak links in the device stack?

**Perovskite Active Layer:** Phase segregation, phase stability, ion migration, thermal decomposition... \( \text{MAPbI}_3 \) replaced with FAMACsPbIBr

**Interfaces:** Band alignment, trapped charges, catalysis, water ingress...

**Contact Layers:** doping, redox, thermal stability...
Li-Free, hydrophobic HTMs

**HTM Wish List**
- Facile synthesis/purification
- Hydrophobic (incl. Li-free)
- Suitable HOMO level
- Easily tunable
- Good hole mobility

**EH44 offers improved hydrophobicity**

Li-Free: Employs predoped HTM as a dopant

HTM + AgTFSI → HTM$^+$TFSI$^-$ + Ag(s)

<table>
<thead>
<tr>
<th>HTM</th>
<th>PCE (%) [max]</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF</th>
<th>SPO (%)</th>
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</thead>
<tbody>
<tr>
<td>spiro Li-TFSI</td>
<td>10.2 [13.3]</td>
<td>17.5</td>
<td>0.99</td>
<td>0.55</td>
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<tr>
<td>EH44 TFSI</td>
<td>10.2 [13.2]</td>
<td>18.6</td>
<td>0.94</td>
<td>0.60</td>
<td>7.9</td>
</tr>
</tbody>
</table>

Optimized EH44 vs. Spiro-OMeTAD

Stability: Spiro vs. EH44

- EH44 helps but doesn’t solve stability
- Dynamic changes in all PV parameters ...
- What about other interface?
  - TiO₂ - most studied photocatalytic semiconductor
  - Substrate drives the crystallization
    - ETL options
      - ZnO, SnO₂, fullerenes

Vertical composition: HTLs and SnO$_2$ vs TiO$_2$

- ToF-SIMS profiles of fresh, full device stacks
- Changes in perovskite active layer observed between TiO$_2$ and SnO$_2$
- Crystallization influenced by substrate

ETL interface: SnO₂ vs TiO₂

- TOF-SIMS
- Changes in TiO₂:
  - A-site distribution (FA, MA, Cs)
  - Implications for: Band structure, photo-carrier dynamics
- Changes in SnO₂:
  - More uniform profiles
  - Less vertical changes after operation

Stable unencapsulated device

Stability improvements to date...
So how has this semiconductor escaped us for so long???

Perovskite crystal

I
Pb
A-site cation
Overcoming Phase Challenge in CsPbX$_3$ Perovskites

Nanocrystals with bright light emission


• Bulk lattice parameter is 6.2894 Å at 360 °C (Temp dependent)

• CsPbI₃ NCs show decreasing lattice constant vs size.

• Trait also seen in other materials, like BaTiO₃, anatase-TiO₂, CdSe, NaYF₄, ...

Ligands required for high temperature, colloidal synthesis

However, these ligands are bulky and insulating

Replacement of ligands:
- Enables layer-by-layer deposition
- Improves charge transport
- Complete removal of ligands leads to agglomeration
PV devices from all-Inorganic Perovskite QDs

- First colloidal perovskite nanocrystal solar cell
- Layer by layer spincoating of QDs with Pb(NO$_3$)$_2$ treatment in MeOAc
- Highest PCE & stabilized power output of any CsPbX$_3$ solar cell
- Unprecedented Voc

Perovskite NC ionic playground

$\text{AMX}_3$

$\text{Pb}^{2+}, \text{Sn}^{2+}, \text{etc.}$

$I^-, \text{Br}^-, \text{Cl}^-$

$\text{Cs}^+, \text{MA}^+, \text{FA}^+$

$x\text{RCOO}^-, y\text{NH}_3\text{R}^+$

Anion exchange simply by mixing 2 types of NCs!

AX salt treatment on CsPbI$_3$ QD films

FAI treatment leads to record QD solar cell

Reasons to be interested in QD perovskites

- More familiar traditional organic solvents (hexane, octane, toluene, chloroform…)
  - Ability to blend with PCBM (reduced hysteresis), other additives, polymers, etc.

- Moves away from the complications that: large grains = better performance
  - Would be hard to implement that in fast printing module production

- No retained solvent, no need to worry about the crystallization dynamics

- Better PLQY, excellent LED potential – enhanced photon recycling

- Ideal solution processed candidate for top cell in multijunction devices
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