Metal Halide Perovskites at the Nanoscale: high quality optoelectronic materials with many unique properties and distinctions from thin film perovskites.

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The rediscovered metal halide perovskite semiconductor system has the potential to be extremely transformative for all optoelectronic devices, especially photovoltaics (PVs). Perovskite semiconductors of the form $APbI_3$ where A is a large +1 charged cation, typically Cs, methylammonium, or formamidinium have had a huge resurgence among materials scientists for outstanding PV properties despite being overlooked for decades. Semiconductors containing the latter two A-site cations listed are *hybrid organic-inorganic materials*, and as such, are far less understood compared to conventional all inorganic or even organic material systems. Regardless of this spotty formal understanding, lead-halide perovskites have very rapidly been optimized to power conversion efficiency levels on par with all other materials even with extensive history of research. Perovskites show a unique tolerance to crystalline defects that cause trouble in most other semiconductors. Therefore the potential offered is that very high efficiency PVs can be fabricated in extremely fast and inexpensive ways, thus offering a revolution for the solar industry and a direct route toward producing the world's energy with a simple and clean technology. Long-term durability of the devices is the critical remaining challenge to be solved.[1] Two examples of major instabilities in device performance are the volatility of the organic cation and the specific crystal habit in which the material embodies.

Nanoscale versions (often termed quantum dots (QDs)) of the all-inorganic metal halide perovskite ($CsPbI_3$) tend to retain the desired perovskite phase due to strain effects at the surface of the QDs whereas conventional films of the same material "relax" to an orthorhombic non-perovskite structure at room temperature. Therefore these QDs potentially solve both of the instability issues. This customizable new nanomaterial system has incredible potential for many applications in optoelectronics, including photovoltaics, LEDs, displays and lasers. This talk will cover several related projects that describe:

1) the phase stability of all-inorganic perovskite QDs

2) surface treatments to manipulate transport in perovskite QD arrays

3) cation exchange-based synthesis of homogeneous alloyed QDs

4) our latest work in QD solar cell device architectures

5) doping of perovskite QD films for manipulating electronic properties (enhanced mobility).

Perovskite QD compositions can be tuned without changing the crystal framework by either direct synthetic methods or by post-synthetic ion exchanges. Particularly, X-site ion exchange in the perovskite QDs with general formula ABX_3 (where A= Cesium-Cs, methylammonium-MA, formamidinium-FA etc.; B= Pb or Sn; X= Cl, Br, I) has shown to be very facile. On the other hand, A-site composition tunability is very limited in these materials, or even in the corresponding thin films.

For example, high FA concentration $Cs_{1-x}FA_xPbI_3$ has not previously been demonstrated in either QDs and thin films, and it has been shown that only compositions with $(1-x)>0.4$ can be realized in the pure usable perovskite phase. This is due to thermal instability of $FAPbI_3$ (crystallizes at around 130 ^{o}C) at temperatures required to crystallize $CsPbI_3$ (above 300 ^{o}C). We will present work on a way in which QDs can overcome this limitation. Simple post synthetic cross-cation exchange reaction between colloidal solutions of $CsPbI_3$ and $FAPbI_3$ nanocrystals occurs just by mixing them at temperatures slightly above the room temperature that enables us to achieve compositions in the whole range of $0<x<1$. This helps us to realize QD compositions that were not known previously even in thin film varieties. The photoluminescence (PL) kinetics studies reveal that the activation energy required to inter-exchange the Cs^+ and FA^+ ions is around 0.65 eV, higher than that for X-site exchange (0.3 eV) in lead halide perovskites. We explored the use of mixed composition perovskite QDs in QD solar cells and will describe the trade-offs found for various compositions.

The fabrication of perovskite QD solar cells requires compact QD films with long range electronic transport. We find distinct differences in the surface chemistry of perovskite QDs compared to previous QD solar cell technology that utilize Pb-chalcogenide QDs. In perovskite QDs, the tunability of transport is far less reliant on perfectly passivated surfaces due in part to the enhanced defect tolerance, however there are still similar strategies that are inspired from PbS solar cells that have proven useful in this newer technology spaces. Ligand exchange processes are developed that retain the high temperature phase in ambient conditions making up the active layer in optoelectronic devices. Such Perovskite QD solar cells with various QD compositions show high V_{OC} of 90% of their maximum in the radiative limit. The perovskite $CsPbI_3$ QD cells operate with a rather remarkable open-circuit voltage of >1.2 volts and have produced power conversion efficiencies over 16%.

Due to the processability differences between perovskite thin films and perovskite QDs, the QD systems enables more complex device structures that can be advantageous for directing energy flow and charge carrier kinetics within the active layer in a device. We have thus developed new device architectures that embody this ability and may offer strategies to further increase the efficiency of solar cells even beyond our current best of 15.5%.

Finally, due to the high surface area of QD films, perovskite QD arrays are explored for ability to manipulate the carrier conduction via surface doping. Due to the previously mentioned high defect tolerance, doping in perovskites requires novel strategies. We have discovered a concentration controlled method of increasing or decreasing the carrier concentration and mobility of photoactive perovskite QD arrays, and demonstrate this ability with photomodulated FET devices.

References
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