Inorganic–Organic Perovskites as Efficient Light Emitting Diode Materials

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Inorganic–Organic Perovskite materials are, broadly defined, as a class of material with a structure depicted in Figure 1. These materials are exceptional solar cell absorbers, mainly because they are simple to make in high quality, have a large carrier diffusion length, and have weakly bound excitons. The conditions that make these materials such fantastic solar cells are tentatively what limits them to the opposite process: efficient radiative recombination of charge carriers.
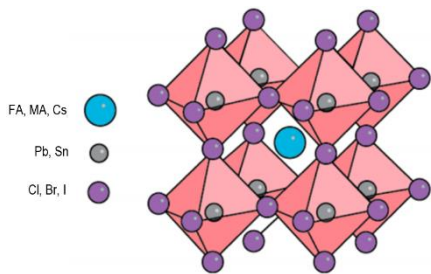

Figure 1: Perovskite structure ABX_3[12]

Despite this limitation, a powerful economic reason to find new ways to cheaply/simply make high quality emissive materials has caused researchers to look at these inorganic-organic perovskite materials.[1-12]

Early attempts to utilize inorganic-organic perovskites as efficient emissive materials were met with many drawbacks. Mainly, room temperature luminescence was near impossible because the weakly bound excitons dissociated too easily at room temperature. An answer to this was to simply confine the charge carriers by synthesizing very thin films of these materials. While this did allow room temperature luminescence and a tunable solution-based synthesis, the quality of the materials was very poor, and as a result their external quantum efficiencies (EQE) was near 0.1%.[2] A film "pinning" process was then developed to improve the film qualities using the same material. In short, an anti-solvent along with a passivating additive were included in the film formation process to boost the crystallization speed and disallow the formation of large grains. As a result, quantum efficiencies were, once again, boosted immensely. Consequently, this required a much higher turn on voltage and overall harsher operating conditions.[3] Despite the progress to develop room temperature, high quality, solution processed luminescent films of these perovskites, improvement was still necessary.

In 2016, Jianpu Wang's group and Ed Sargent's group simultaneously utilized a lower dimensional 'version' of the 3D lead perovskite known as Quasi-2D perovskites to produce LED's with efficiencies of 8.5% and 11%, respectively.[6,7] They are a discretely layered material with a specific number of PbX_4^{2-} unit cells "n" between two layers of bulky hydrophobic ammonium

Figure 2: Visualization of Quasi-2D Perovskite Unit Cells with varying $<n>$[5]

cations – a unit cell and depiction of layer thickness can be seen in Figure 2 with a structure $L_2A_{n+1}M_nX_{3n+1}$. L is the hydrophobic organic cation, A is a small cation like methylammonium or formadinium, M is Lead (Pb) and X is a halide, typically I. The hydrophobic layer, typically a benzyl ammonium cation, cannot fit well into the corner of the perovskite lattice and terminates the crystalline growth at that point. The existence of a finite number of layers of perovskite atoms afford that the smaller the layer, the higher the bandgap will be based on quantum confinement. This large dielectric mismatch between the perovskite and hydrophobic layers greatly strengthens the exciton binding energy meaning room temperature electroluminescence can be achieved.[4,5] These quasi-2d perovskites also produce high quality films with extraordinarily small grain sizes which mitigates trap defects to overall improve

efficiency. Their synthesis is also very simple wherein a precursor mixture of (PbI_2, MAI, and PEAI) are spin coated onto a substrate and then an anti-solvent is added to afford smooth film formation. Both groups attempted to understand the mechanics of how these materials work and manage to produce such high efficiencies despite the presence of bulky hydrophobic molecules that would theoretically limit charge transport between the layers.

A key point to make is that in the process of making one of these films, despite aiming towards a specific layer thickness, a mixture of layers is always achieved. This mixture results in an absorption spectrum where the individual band gaps associated with different "n" thicknesses are present, and because of quantum confinement effects the smaller "n" layers have higher bandgaps than the lower "n" layers. Interestingly, most of the absorption occurs in higher band gap layers, whereas photoluminescence is always most intense at the smallest layers, indicating that a series of energy transfer events occur in these materials. Using photoluminescent and absorption spectroscopy, the prepared quasi-2d films were thoroughly characterized and their unique photophysical properties were explored.[7] Ultra-Fast transient absorption measurements on a film of $(PEA)_2(MA)_2Pb_3I_{10}$ (<n>=3) indicate that at very short time scales there exist an intense bleaching at exactly the absorption peak related to layers of n=2-4, but at longer time scales the bleaching peaks are focused on larger "n" layers. Jianpu Wang's group provided higher resolution at much shorter time scales to allow a true visualization of the energy transfer process. This transfer process is shown to be much faster than the diffusion process out of the band edges and vastly reduces the chance of defect or grain boundary trapping. Time resolved Photoluminescence of the films produced by Wang's group also confirm this idea.[6]

Preparing LED devices of these materials proved that the efficient energy transfer mechanism is still applicable when the charge carrier generation is of a different source. Much of the characterization done by the Sargent and Wang group were photoexcitation characterization methods and did not perform a rigorous analysis of the possible different mechanisms between the two. Based on the Sargent group's results, it implies that what you choose as your <n> greatly affects performance of the LED's, where Wang's group failed to recognize this importance. An optimum <n> is crucial for high efficiency of LED.[8] Neither group did extensive structural analysis beyond EDX or XPS which limits the understanding of what the layer distribution looks like or where they are arranged as these are ensemble measurements. This information would be invaluable, however, to designing optimized devices.

Figure 3: Vertical preferred orientation of perovskite films and random horizontal orientation[9]

Work by Shang et al on the device architecture showed that depending on which side of a prepared LED device you excite or inject charge carriers into, a different luminescent spectrum can be observed.[9] The high relative intensities of higher to low "n" layers implies that perpendicular to the substrate, an even distribution from low to high "n" layers exists. They then use Kelvin Force Probe microscopy technique to analyze the surface potential of these films. A random, distribution of higher "n" domains exists on the surface implying an overall architecture that can be seen in Figure 3. These results imply a minimum thickness, but not necessarily minimum area is required to achieve good performance – good news for display technologies.

In conclusion, a desire for solution-based LED materials has spurred interest in a class of Inorganic-Organic Lead Halide perovskites called Quasi-2D Perovskites wherein films with

quantized layer thicknesses leads to very interesting photophysical properties. Their synthesis is facile and their performance as LED's depends strongly upon the presence of mixture of layers in films with very small grain sizes. The small grain sizes and uniform coverage ensure that defects will not a dominant decay mechanism, and the self-assembled quantum well type structures that result ensure efficient energy transfer from low to high "n" layers which greatly improves performance. Other colors than red have been pursued using this concept, with green being very successful. However, blue might be a challenge because the funneling concept might not apply. These materials do, however, present a very interesting type of material that satisfies the main conditions for high efficiency electroluminescence in solution processed conditions.[10,11]

1. Zhao, X.; Ng, J.D.A.; Friend, R.H.; Tan, Z.K. *ACS Photonics.* **2018**, *5* (10), 3866–3875
2. Tan, Z.K.; Moghaddam, R.S.; Lai, M.L.; Docampo, P.; Higler, R.; Deschler, F.; Price, M.; Sadhanala, A.; Pazos, L.M.; Credgington, D.; Hanusch, F.; Bein, T.; Snaith, H.J.; Friend, R.H. *Nature,* **2014,** *9,* 687-692.
3. Cho, H.; Jeong, S.-H.; Park, M.-H.; Kim, Y.-H.; Wolf, C.; Lee, C.-L.; Heo, J. H.; Sadhanala, A.; Myoung, N.; Yoo, S.; Im, S. H.; Friend, R. H.; Lee, T. -W. *Science* **2015,** *350*(6265), 1222-1225
4. Calabrese, J.; Jones, N.L.; Harlow, R.L.; Thorn, D.L.; Wang, Y. *J. Am. Chem. Soc.* **1991,** *113(6)*, 2328-2330
5. Smith, I. C.; Hoke, E. T.; Solis-Ibarra, D.; McGehee, M. D.; Karunadasa, H. I. *Angew. Chem*. **2014**, *126*, 11414 –11417
6. Wang, N.; Cheng, L.; Ge, R.; Zhang, S.; Miao, Y.; Zou, W.; Yi, C.; Sun, Y.; Cao, Y.; Yang, R.; Wei, Y.; Guo, Q.; Ke, Y.; Yu, M.; Jin, Y.; Liu, Y.; Ding, Q.; Di, D.; Yang, L.; Xing, G.; Tian, H.; Jin, C.; Gao, F.; Friend, R.H.; Wang, J. L.; Huang, W. *Nature Photonics* **2016,** *10* (11), 699-704.
7. Yuan, M.; Quan, L.N.; Comin, R.; Walters, G.; Sabatini, R.; Voznyy, O.; Hoogland, S.; Zhao, Y.; Beauregard, E.M.; Kanjanaboos, P.; Lu, Z.; Kim, D.H.; Sargent, E.H. *Nat. Nanotechnol.* **2016**, *11,* 872-879.
8. Yantara, N.; Bruno, A.; Iqbal, A.; Jamaludin, N.F.; Soci, C.; Mhaisalkar, S.; Mathews, N. *Adv. Funct. Mater.* **2018**, *30*, 1800818.
9. Shang, Q.; Wang, Y.; Zhong, Y.; Mi, Y.; Qin, L.; Zhao, Y.; Qiu, X.; Liu, X.; Zhang *J. Phys. Chem. Lett.* **2017**, *8*, 4431−4438
10. Yang, X.; Zhang, X.; Deng, J.; Chu, Z.; Jiang, Q.; Meng, J.; Wang, P.; Zhang, L.; Yin, Z.; You, J. *Nat. Comm.* **2018**, *5*, 570-578.
11. Chen, L.l; Cao, Y.; Ge, R.; Wei, Y-Q.; Wang, N-N.; Wang, J-P.; Huang, W. *Chinese Chemical Letters.* **2017**, *28*, 29-31.
12. Green, M. A.; Ho-Baillie, A. *ACS Energy Lett.*, **2017**, *2* (4), 822–830