Light emission from perovskite materials

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I. INTRODUCTION

Lead-halide perovskites have rapidly evolved from chemical curiosities for photovoltaics in 2009 to a major contender for a wide range of optoelectronic devices only a decade later.[1,2] Among the key enabling properties are high absorption coefficients, high photoluminescence quantum yields (PLQYs) approaching unity, long charge-carrier diffusion lengths, and low Urbach energies of 30 meV or lower.[3–5] With this set of properties, lead-halide perovskites have significant potential for light-emission applications, particularly since their bandgap can be tuned over the entire visible wavelength range by changing their composition or through quantum confinement.[4–6] These applications include light-emitting diodes (LEDs) for lighting and ultrahigh definition displays, as well as low-cost solid-state lasers. Moreover, the efficient luminescence from lead-halide perovskites provides a valuable tool to gain fundamental insights into the kinetics of charge-carriers in these materials and how these kinetics are influenced by structure and processing. Despite the rapid progress in the understanding and engineering of light-emission from these materials, the research field is still in its early stages in many areas. This special issue brings together a collection of research articles and perspectives focusing on some of the important outstanding questions and challenges in the field. Here, we highlight the key discussions made on the photophysics of perovskite emitters, composition engineering for high efficiency perovskite LEDs, white-light devices, and lasing in perovskites. We emphasize some of the important research questions moving forward.

II. PHOTOPHYSICS OF PEROVSKITE LIGHT-EMITTERS

Lead-halide perovskites demonstrate an unusual tolerance to point defects, in which long charge-carrier lifetimes >100 ns can be achieved despite having orders of magnitude higher defect densities than traditional semiconductors.[7] This is partly due to most defects being shallow, yielding lower Shockley–Read–Hall recombination rates than if they were deep within the bandgap.[7] Nevertheless, deep traps do exist and need to be eliminated (e.g., through passivation)[8] in order to achieve high photoluminescence quantum yields. In particular, the microstructure plays an important role in charge-carrier recombination, and it has been found that perovskite grain boundaries have lower luminescence and photoluminescence lifetimes than those of the bulk of the grain.[9] More recently, Liu *et al.* investigated the role of ferroelastic twin domains in luminescence in methylammonium lead iodide ($MAPbI_3$) perovskite by correlating the scanning electron microscopy measurements of the morphology with confocal photoluminescence measurements over the same area.[10] Although some works suggest that twin domains affect charge separation and transport, the measurements made by Liu *et al.* showed that the ferroelastic twin boundaries have negligible effects on photoluminescence or on the electronic properties. However, they did find variations in luminescence in neighboring twin domains, but these were attributed to variations in light–matter interactions.[10]

Beyond the influence of the microstructure, the role of contact layers in carrier kinetics in perovskite emitters is important to understand in order to maximize the efficiency of light-emitting devices.[11,12] Trinh *et al.* examined the role of TiO_2 in fluorescence intermittency (also known as "blinking") in single formamidinium lead bromide ($FAPbBr_3$) perovskite quantum dots.[13] Under pulsed excitation at 380 nm wavelength, $FAPbBr_3$ single dots on glass exhibited rapid variations in photoluminescence between high (on) and low (off, comparable to background) levels. However, this blinking was found to be suppressed when the quantum dots were on TiO_2, which was attributed to electrons from TiO_2 filling the trap states in the quantum dots responsible for blinking.[13]

Suárez *et al.* took the characterization of perovskite nanocrystals further and developed a method to characterize the excitonic transitions in individual nanocrystals.[14] This was achieved through optical microscopy of perovskite ($CsPbBr_3$) nanocrystals mounted on the antenna of TiO_2, which has a high dielectric constant. The TiO_2 antenna formed Mie resonators that enhanced the absorption and emission from the nanocrystals. This approach allows the characterization of luminescence below the diffraction limit, which is important for investigating the photophysics of individual nanocrystals.[14]

III. MATERIALS AND INTERFACE ENGINEERING FOR LIGHT-EMITTING DIODES

In perovskite LEDs, it is important to confine electrons and holes in order to improve the device efficiency, particularly given the low exciton binding energy of three-dimensional perovskites.[15] Apart from the use of nanocrystals, this has been achieved in thin films by reducing the dimensionality.[16] Sun *et al.* discussed the potential of Ruddlesden–Popper (i.e., two-dimensional) perovskite thin films for LEDs.[17] The 3D symmetry of the perovskites is broken by introducing long alkylammonium chains that assemble between the perovskite layers and act as barriers against moisture ingress, thus improving the environmental stability. Solution processing perovskites containing these long alkylammonium chains can result in multiple perovskite dimensionalities in which lower-dimensional perovskites have wider bandgaps. As a result, injected charges can be funneled down in energy to the highest dimensionality perovskite, in which the charges would be confined and recombine more efficiently. This strategy has yielded near-infrared perovskite LEDs with >20% external quantum efficiency (EQE).[18,19] However, the remaining challenges are the (1) limited stability of the LEDs, (2) need to replicate the successes of near-infrared emitters in blue emitters, (3) replacement of Pb with less harmful elements and still achieve high performance, and (4) development of large-area perovskite LEDs.[17] Another important challenge with low dimensional perovskites is that the energy level (i.e., valence band maximum) for hole injection is deeper than the work function of common hole-injection materials, such as PEDOT:PSS (work function of 5.0 eV).[20] Ricciardulli *et al.* developed a hole-doped triarylamine-fluorene copolymer (*p*-pTFF-C_2F_5SIS) as an alternative that has a higher work function of 5.85 eV. This resulted in improved efficiency of hole injection into a emitter comprising a quasi-2D/3D perovskite blended with a wide bandgap poly(2-hydroxyethyl methacrylate) polymer.[20]

Luo *et al.* discussed the current status and challenges of achieving efficient blue perovskite LEDs.[21] Efficient blue emitters are necessary for full perovskite-based displays, as well as for white lighting.[22] The wider bandgap of blue-emitters results in an increased likelihood of deep traps occurring, as well as large charge injection barriers, both of which contribute to blue perovskite LEDs lagging behind in EQE (up to 6.3% at 470 nm wavelength,[23] and very recently 12.3% at 475-480 nm wavelength[30]) compared to their green, red, and near-infrared counterparts, which have >20% EQE reported.[21] While passivating defects and the use of nanoplatelet structures to blue-shift the emission through quantum confinement are promising strategies, important challenges are the limited stability of blue LEDs and the spectral instability of mixed-halide (e.g., Cl/Br) compositions under applied bias.[21]

Finally, most reports on perovskite LEDs use solution processing to fabricate either thin films or nanostructured materials. For large-area manufacturing, evaporation may be more appealing. Xie *et al.* reported the fabrication of cesium lead bromide LEDs with the emitter deposited by co-evaporation of CsBr and $PbBr_2$. They showed how co-evaporation allows control over the ratio of CsBr:$PbBr_2$, which has a significant effect on the PLQY of the thin films and EQE of the devices. The highest PLQYs (of 5.1%) and EQEs (of 1.1%) were achieved using the highest CsBr:$PbBr_2$ ratio of 5:1. These LEDs were green emitting (at 531 nm wavelength) with a narrow full-width at half maximum of the electroluminescence peak of 21 nm.[24]

IV. WHITE-LIGHT DEVICES

The high absorption coefficient and PLQYs of lead-halide perovskites have prompted several groups to investigate them as phosphors for down-converting UV light (e.g., from a standard GaN LED) for white light emission. Worku *et al.* explored this in their perspective and explain how lead-halide perovskites offer the potential to avoid the need for rare-earth dopants (which are commonly used in current commercially available phosphors) while enabling fine control over the quality of the white light emitted.[25] The key properties of white light LEDs are the (1) color rendering index (CRI; 0–100), which quantifies the ability of light sources to faithfully show the colors of objects that would be observed under natural light, (2) correlated color temperature (CCT; units of K) with higher CCTs describing "colder" or bluer white light, and (3) luminous efficacy (units of lm W^{-1}) describing the ratio of the luminous flux produced to the electrical power input.[25,26] Currently, the strategies explored have been to combine single-wavelength perovskite down-converters with a broadband-emitting phosphor (e.g., YAG:Ce) or to develop perovskites that directly give broadband emission, such as through the recombination of self-trapped excitons. These strategies have given CRI values approaching 100, albeit currently with lower luminous efficacies than standard phosphors.[25] However, an important finding is that efficient white-light perovskite phosphors could be achieved in lead-free perovskite-inspired materials, some of which have demonstrated improved stability over their lead-based counterparts (e.g., $Cs_2Ag_{0.6}Na_{0.4}InCl_6$ doped with 0.04% Bi).[27] Furthermore, the emitters (both lead-halide perovskites and lead-free alternatives) can be embedded within encapsulating layers (e.g., a polymer matrix) to improve the stability of the phosphors under ambient or moist conditions.[28]

V. TOWARDS ELECTRICALLY DRIVEN LASING

Although lead-halide perovskites have been demonstrated to be promising optical-gain media, achieving electrically pumped lasing has proven elusive. Gunnarsson *et al.* discussed the key challenges to realizing perovskite laser diodes. Namely, these are (1) thermally induced degradation of the perovskite and reductions in the PLQY due to Joule heating, (2) quenching of the luminescence in the perovskite due to the application of an electric field, (3) imbalanced injection of electrons and holes, and (4) Auger recombination, which will play a role due to the high current densities that is needed for electrically pumped lasing.[29] Joule heating is identified to be particularly harmful and would prevent the high current densities ($>$100 A cm^{-2}) needed to reach the lasing threshold before the emission is quenched. Currently, it is still unknown whether electrically pumped lasing could be realized, but achieving this could result in low-cost, non-epitaxial laser diodes that could be used in flexible and lightweight devices.[29]

VI. CONCLUSIONS

In summary, this special issue gives a taste of the breadth and diversity of research into light emission in lead-halide perovskites, which has only emerged in the past few years. Some of the successes of the field are shown, as well as glimpses into novel applications of perovskites. The discussions of the current challenges in the field contained within this issue will be important for guiding future efforts.

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