Light Emitting Diodes Based on Metal Halide Perovskites and Beyond

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Abstract

Light emitting diodes (LEDs) have wide applications from full-color displays to solid-state lighting. Numerous types of luminescent materials have been explored for LEDs, ranging from inorganic semiconductors to metal complexes and quantum dots. Despite the rapid pace of development, LEDs have not achieved their full potentials in terms of performance and cost efficiency. Identifying new eco-friendly materials for LEDs is of great interest. Recently, metal halide perovskites and perovskite-related hybrid materials have emerged as new generation luminescent materials with unique optoelectronic properties. Here, some of our recent development of LEDs based on metal halide perovskites and perovskite-related materials will be discussed.

Author Keywords

Light Emitting Diodes; Metal Halide Perovskites, Organic Metal Halide Hybrids, Surface Passivation, Organic Semiconductors.

1. Introduction

Electrically driven light emitting diodes (LEDs) have experienced tremendous development over the last decades with wide applications in displays and solid-state lighting. Numerous types of light emitting materials and device configurations have been explored, including epitaxially grown inorganic semiconductors based LEDs,[1] organic LEDs (OLEDs),[2] and quantum dot LEDs (QLEDs).[3] Despite their remarkable rapid pace of development, electrically driven LEDs have not yet come close to achieving their full potentials. Significant work remains to be done to further improve performance and reduce costs.

Recently, metal halide perovskites (MHPs) have emerged as new generation light emitters for electrically driven LEDs (PeLEDs), for their highly tunable narrow emissions, excellent charge transport properties, defect tolerance, and facile solution processability.[4] Typical MHPs have a three-dimensional structure (3D) with a chemical formula of ABX_3, where A represents the monovalent cation, such as methylammonium ($CH_3NH_3^+$) and Cs^+, B a divalent metal ion, such as Pb^{2+} and Sn^{2+}, and X a halide anion (Cl^-, Br^-, I^-, or their mixtures). In 2014, room temperature PeLEDs were demonstrated with EQEs of less than 1%,[5] which share a similar device structure as those of OLEDs and QLEDs, wherein light emitting layer is sandwiched between electron and hole transport layers (ETL and HTL) (Figure 1). Since then, remarkable progress has been achieved in the development and study of light emitting MHP materials and devices. In particular, highly efficient green, red, and near-infrared (NIR) PeLEDs with internal quantum efficiencies (IQEs) approaching the theoretical maxima and EQEs of more than 20% have been demonstrated.[6] While significant progress has also been achieved in blue PeLEDs, their performance still lags behind those of green, red, and NIR PeLEDs, largely due to the inferior change transfer and energy level alignment. Developing efficient blue PeLEDs remains one of the major challenges in the field.

Another issue related to PeLEDs based on 3D MHPs is the presence of toxic lead in these devices, a major environmental and health concern that could limit their wide commercialization. In searching for efficient lead-free perovskite-related light emitting materials with high stability, great achievements have been made recently in zero-dimensional (0D) organic metal halide hybrids (OMHHs),[7] which contain light emitting metal halide polyhedra fully isolated and surrounded by bulky organic cations to exhibit broadband emissions with high photoluminescence quantum efficiencies (PLQEs) of up to near-unity (Figure 1). However, applications of 0D OMHHs in electroluminescent devices have been significantly underexplored, due to the low conductivity of organic cations resulting in inferior change transfer and energy level alignment, the same issues occurring in many blue PeLEDs.

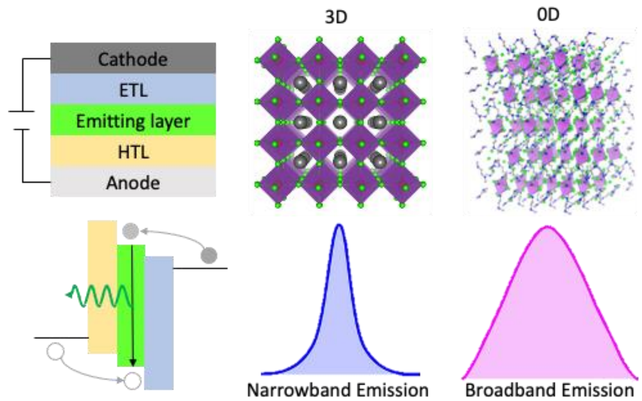

Figure 1. Typical device structure of an electrically driven LED; its operation with holes and electrons injecting into HTL and ETL, transporting and recombining to form excitons in the interfaces and emitting layer to emit light; the crystal structures of 3D MHPs and 0D OMHHs; the typical emission features: narrowband emission from 3D MHPs and broadband emission from 0D OMHHs.

To address these common issues of low conductivity and poor energy alignment in blue PeLEDs and LEDs based on 0D OMHHs, we have recently developed organic semiconducting salts, for instance, triphenyl(9-phenyl-9H-carbazol-3-yl) phosphonium bromide (TPPcarzBr), to serve as surface passivation agent for blue emitting perovskite nanocrystals, i.e. $CsPbBr_3$ nanoplatelets (NPLs), and form conductive 0D OMHHs, i.e. $TPPcarzSbBr_4$. As compared to well-known tetraphenylphosphonium bromide (TPPBr), TPPcarzBr with the inclusion of a charge transport phenylcarbazole unit possesses lower bandgap and higher conductivity. With solution processed emitting layers based on $CsPbBr_3$ NPLs and 0D $TPPcarzSbBr_4$, efficient and stable LEDs have been demonstrated.[8,9]

2. Results and Discussion

By using TPPcarzBr and $TPPcarz_2SO_4$, in addition to conventional insulating oleylamine, for surface treatment, highly uniform $CsPbBr_3$ NPLs with thickness of 3 units of $PbBr_6^{4-}$ octahedra (around 2 nm) and lateral size of up to 300 nm have been developed for the first time (Figure 2), following a modified colloidal synthesis method. These $TPPcarz_2SO_4$ and TPPcarzBr treated $CsPbBr_3$ NPLs exhibit a blue emission peaked at 455 nm with a high PLQE of 82% and a remarkably low full width at half maximum (FWHM) of 13 nm (Figure 2). Solution processed thin films based on these new $CsPbBr_3$ NPLs exhibit excellent uniformity and smoothness, thanks to the relatively high viscosity of solution and stable dispersion of $CsPbBr_3$ NPLs. The thin films also possess excellent stability under continuous UV irradiation (365 nm, 40 mW/cm^2), with a small intensity reduction after 60 min and no shift in the emission peak after 180 min. More importantly, $TPPcarz^+$, as energetically aligned conductive ligand, has enabled improvement of charge carrier mobility by orders of magnitude for thin films based on $CsPbBr_3$ NPLs, which prevents charge accumulation with balanced charge injection at the interfaces, circumventing the key bottleneck of low efficiency and inferior stability of blue PeLEDs. With thin films based on new $CsPbBr_3$ NPLs as emitting layer, blue PeLEDs (Figure 2) have been fabricated with a simple device structure, ITO/PEDOT:PSS/poly-TPD)/$CsPbBr_3$ NPLs/TPBi/LiF/Al, which exhibit a maximum luminance of 1511 cd m^{-2} and an EQE of 4.15 %, the highest values achieved to date for pure blue PeLEDs based on $CsPbBr_3$ NPLs.

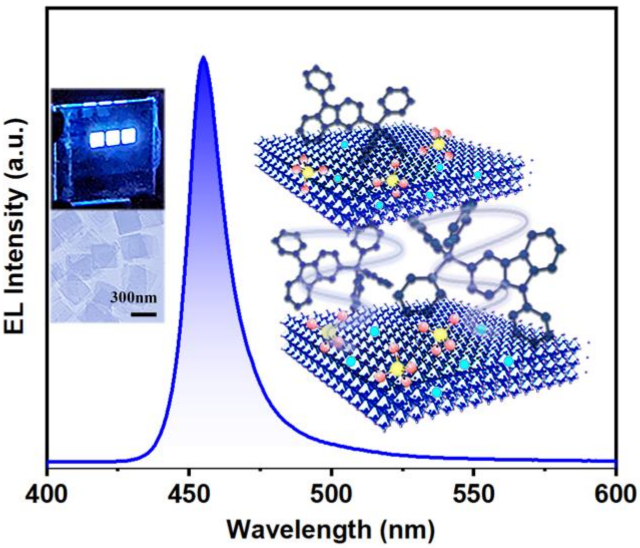

Figure 2. Blue PeLEDs (emission peaked at 455 nm with an FWHM of 13 nm) based on organic semiconducting ligands ($TPPcarz^+$) passivated $CsPbBr_3$ NPLs (thickness of around 2 nm and lateral size of up to 300 nm).

For 0D OMHHs, replacing conventional insulating organic cations with semiconducting ones allows for the development of electroactive light emitters with near unity PLQEs. By reacting TPPcarzBr with $SbBr_3$, we have prepared 0D $TPPcarzSbBr_4$ in both single crystal and thin film forms (Figure 3), which exhibit red emission peaked at 653 nm with an FWHM of 141 nm and PLQEs of 93.8% and 86.1%, respectively. Solution processed $TPPcarzSbBr_4$ thin films exhibit excellent uniformity and smoothness (Figure 3), with a root mean square roughness of around 0.038nm, a sufficiently low value needed for device integration. They are also found to exhibit high thermal and atmosphere stability, maintaining the same photoluminescence after 2 hours on the top of a 150 °C hot plate and 6 months' storage in air. The complete site-isolation of light emitting antimony bromide dimer anions ($Sb_2Br_8^{2-}$) by semiconducting $TPPcarz^+$ cations enables a perfect "host-dopant" structure with efficient charge injection, transport, and recombination. The hole and electron charge carrier mobilities of solution processed $TPPcarzSbBr_4$ thin films are determined to be 1.3×10^{-6} $cm^2\ V^{-1}s^{-1}$ and 3.2×10^{-6} $cm^2\ V^{-1}s^{-1}$, respectively, which are much higher than those of previously reported 0D OMHHs. Using solution processed $TPPcarzSbBr_4$ thin films as light emitting layer, red LEDs (Figure 3) have been fabricated to exhibit an EQE of 5.12%, a peak luminance of 5957 cd m^{-2}, and a current efficiency of 14.2 cd A^{-1}, which are the best values reported to date for LEDs based on 0D OMHHs. The emphasis of this work is to establish the concept of introducing semiconducting organic cations to improve the performance of 0D OMHHs in electronic devices. We believe that the device efficiency and stability can be significantly boosted with appropriate device engineering.

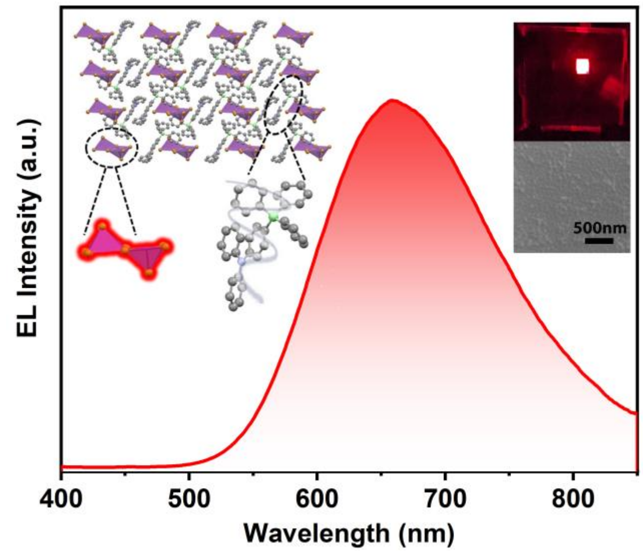

Figure 2. Red LEDs (emission centered at 653 nm with an FWHM of 141 nm) based on solution processed 0D $TPPcarzSbBr_4$ thin films.

3. Impact of Our Research

By exploring novel molecular engineering approaches, we aim to enhance the efficiency, stability, and performance of LEDs based on metal halide perovskites and perovskite-related materials. Our research has gained new insights into materials chemistry, thin film processing, and device physics for this emerging class of hybrid materials, paving the way for the development of next-generation LEDs with widespread applications in lighting, displays, and beyond.

4. Acknowledgements

The author thanks the support from the National Science Foundation (ECCS-2210902).

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