

High Efficiency and Durability from Perovskite–Organic Hybrid Light-Emitting Diodes

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ABSTRACT

Perovskite light-emitting diodes are promising for next-generation lighting and displays. However, the nature of how excitons affect performance is still not clear in perovskite and quasi-two-dimensional (2D) perovskite-based devices. Here, we show that triplet excitons are key to efficient emission in green quasi-2D perovskite devices and that quenching of triplets by the organic cation is a major loss path. Employing an organic cation with a high triplet energy level (phenylethylammonium) in a quasi-2D perovskite based on formamidinium lead bromide yields efficient harvesting of triplets. Furthermore, we show that upconversion of triplets to singlets can occur, making 100% harvesting of electrically generated excitons potentially possible.

1 INTRODUCTION

Perovskites are extremely attractive for electronics applications because they can be processed easily at low cost and tuned to achieve a wide range of electrical and optical properties. Although a number of reports of high-performance perovskite solar cells and field-effect transistors already exist, the performance of perovskite light-emitting diodes (PeLEDs) still has considerable room for improvement. The first PeLEDs operating at room temperature used three-dimensional (3D) methylammonium lead halide perovskites such as $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$, $\text{CH}_3\text{NH}_3\text{PbBr}_3$ and $\text{CH}_3\text{NH}_3\text{PbBr}_2\text{I}$ as the emissive layer [1], but the focus has largely switched to quasi-two-

dimensional (2D) perovskite films, which contain a distribution of grains with dimensionality ranging from 2D to 3D [2]. Quasi-2D perovskites take advantage of a higher exciton binding energy to more easily generate electron–hole pairs, as excitons, in the low-dimensionality grains, and these excitons then cascade down to the high-dimensionality grains for highly efficient radiative recombination.

Using such materials, an external quantum efficiency (EQE) of 8.8% was obtained in the near-infrared from $\text{PEA}_2(\text{CH}_3\text{NH}_3)_{n-1}\text{PbI}_{3n+1}$ (PEA, phenylethylammonium), with an average order n of $\langle n \rangle = 5$ [2], and an EQE of 7.4% was obtained in green PeLEDs using $\text{PEA}_2(\text{CH}_3\text{NH}_3)_{n-1}\text{PbBr}_{3n+1}$ [3]. Adoption of 1-naphthylmethylamine iodide to form self-organized multiple quantum wells of formamidinium (FA)-based perovskite yielded an EQE of 11.7% with an electroluminescence (EL) emission peak at 763 nm, but switching the halide to Br to produce green emission resulted in an efficiency of only 0.1% [4]. The use of longer-chain organic cations yielded emission peaking at 513 nm with an EQE of 9.3% and current efficiency of 17.1 cd A^{−1} for the methylammonium lead bromide system [5]. Despite these advances in PeLEDs, the vast difference in EQE for green emission (a key colour for displays and other applications) for different organic cations is not understood, and the EQE values for green devices are still below those of near-infrared PeLEDs and state-of-the-art organic LEDs, which can approach 30% [6].

Although the management of singlet and triplet

excitons is fundamental to the design of efficient organic LEDs, similar considerations have not been discussed for PeLEDs, and the understanding of the excitonic nature of the system remains basic. In green quasi-2D PeLEDs, inorganic layers of corner-sharing $[\text{PbBr}_6]^{4-}$ octahedra are most commonly used. The inorganic layer $[\text{PbBr}_6]^{4-}$ has a Γ_5 singlet state at 3.01 eV and two triplet states of Γ_1 and Γ_2 at 2.99 eV [7]. The energy gap between the singlet and triplet states is small (approximately equal to the thermal energy at room temperature) because of the heavy metal effect. According to spin statistics, electrical excitation is expected to produce three triplets for every singlet. Although singlets generated in the lower-dimensionality perovskite grains can be efficiently transferred by Förster energy transfer over long distances to the higher-dimensionality perovskites, where emission occurs, transfer of triplet excitons is only possible by Dexter energy transfer over short distances. Thus, we propose that accounting for the dynamics of both singlets and triplets is key for the design of highly efficient PeLEDs.

Here, we show that singlet and triplet excitons separated by an extremely small energy gap exist in quasi-2D PeLEDs under electrical excitation. In quasi-2D PeLEDs employing an organic cation (PEA) with a high triplet energy level, triplet excitons can be efficiently harvested. On the other hand, the use of an organic cation with a low triplet energy (1-naphthylmethylamine, NMA) results in poor performance because of the transfer of triplets away from the radiative recombination centres, leading to non-radiative recombination.

2 Results and discussion

2.1 PeLEDs with triplet management [8]

To demonstrate the impact of these findings on device performance, we fabricated PeLEDs with the following architectures. Quasi-2D perovskite films (thickness of 150 nm) were spin-cast from a precursor solution onto indium tin oxide (ITO) coated with a hole-transporting layer of poly(N-vinylcarbazole) (PVK). The two perovskite films based on PEA and NMA were continuous, with similar morphologies. A 40-nm-thick electron-transporting layer of 1,3,5-tris(1-phenyl-1H-benzo[d]imidazol-2-yl)benzene (TPBi) and an electrode of LiF (0.8 nm)/Al (100 nm) were deposited under high vacuum. Finally, the devices were encapsulated in a nitrogen glove box with a glass cap and ultraviolet sealant. Except for ITO cleaning, all fabrication procedures were done without exposure to ambient air. We thus assume that the effects of the external environment, such as moisture and oxygen, on perovskite quality and device performance can be excluded. Both PEA- and NMA-based perovskites have similar valence and conduction band levels, so interfacial energetic alignment for hole and

electron injection is similar from the PVK and TPBi layers, respectively

The NMA- and PEA-based PeLEDs emitted green EL with peak wavelengths of 531 and 527 nm, respectively, and the same FWHM value of 21 nm. The EL corresponded to Commission Internationale de L'Éclairage (CIE) 1931 coordinates of (0.20, 0.75) and (0.18, 0.76) for NMA- and PEA-based PeLEDs, respectively. The NMA-based PeLEDs had a maximum luminance of 500 cd m^{-2} at 6 V, while the PEA-based PeLEDs exhibited a higher brightness of 5,200 cd m^{-2} at the same voltage. Furthermore, the maximum EQE and current efficiency of the PEA-based PeLEDs (12.4% and 52.1 cd A^{-1}) were more than three times those of the NMA-based devices (3.4% and 16.3 cd A^{-1}). The devices were highly reproducible with maximum EQE (averaged over 60 devices) of $2.5 \pm 1.2\%$ and $11.6 \pm 1.0\%$ for NMA and PEA-based PeLEDs, respectively. We attributed the higher EQE in the PEA-based devices compared to the NMA-based devices to efficient harvesting of triplet excitons because of the triplet energy level of PEA lying at a shallower position. The half lifetime of PEA-based devices was low at around 1.5 h. We need a further study to improve the operational durability of PeLEDs through an understanding of their degradation mechanisms. Figure 1 displays a picture of a working PEA-based PeLED with efficient EL.

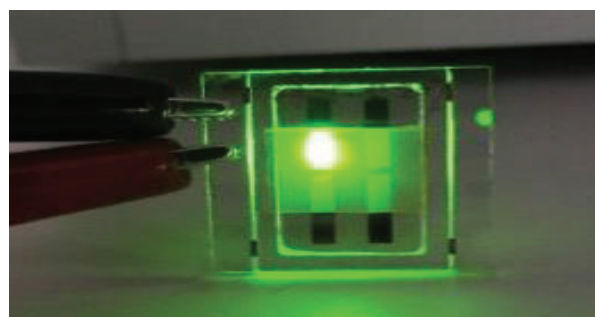


Figure 1. Picture of an example PEA-based quasi-2D PeLED under electrical operation. Efficient EL was realized by managing triplets formed in perovskites.

2.2 Operational durability of PeLEDs [9]

PeLEDs show efficient EL, with EQE being comparable to that of state-of-the-art organic LEDs. However, the operational durability of PeLEDs is still very low and, therefore, needs to be improved for future practical applications through the clarification of their basic degradation mechanisms. In this study, we investigated the durability of quasi-2D perovskite films under three different conditions, i.e., carrier injection only, photoexcitation only, and photoexcitation in combination with carrier injection. As a result of the aforementioned

comparison, we found that excited states (Wannier excitons) formed in quasi-2D perovskite films by photoexcitation are relatively unstable. On the other hand, no degradation of quasi-2D perovskite films was observed when electrons or holes were injected without the formation of excited states. The unstable excited states were associated with the change from the quasi-2D phase with high PL quantum yield to the three-dimensional phase with low PL quantum yield and the formation of metallic lead working as an excited-state quencher in films. Furthermore, the excited-state stability became worse when the excited states and the charge carriers coexisted in films. This would be one of the reasons for the low stability of quasi-2D PeLEDs under continuous electrical operation.

2.3 Optical continuous-wave lasing from perovskite films [10]

Quasi-2D perovskite films are also promising gain media for lasing applications because of their low cost, tunable colour, excellent stability and solution processability. Optically pumped continuous-wave (CW) lasing is highly desired for practical applications in high-density integrated optoelectronics devices and constitutes a key step towards electrically pumped perovskite lasers. However, CW lasing has not yet been realized at room temperature because of the “lasing death” phenomenon (the abrupt termination of lasing under CW optical pumping), the cause of which remains unknown. Here we studied lead halide-based quasi-2D perovskite films with different organic cations and observed that long-lived triplet excitons considerably impeded population inversion during amplified spontaneous emission and optically pumped pulsed and CW lasing. Our results indicate that singlet–triplet exciton annihilation is a possible intrinsic mechanism causing lasing death. By using a distributed-feedback cavity with a high quality factor and applying triplet management strategies, we achieved stable green quasi-2D perovskite lasers under CW optical pumping in air at room temperature (Fig. 2). We expect that our findings will pave the way to the realization of future current-injection perovskite lasers.

3 CONCLUSIONS

In 1994, first PeLEDs were found from Kyushu University. Unfortunately, these first PeLEDs were difficult to operate at room temperature. Efficient EL was detected only at low temperature [11]. Recently, PeLEDs began to show EL even at room temperature [1]. However, there are several issues remaining in PeLEDs. In our group of Kyushu University, we demonstrated that EQE was improved by four-fold by managing the triples formed in

quasi-2D PeLEDs. Although EQE is high, the operational durability of PeLEDs is problematic. We found that excited-states of quasi-2D perovskite films became unstable if the excited states coexist with charge carrier injected from external electrodes. Additionally, we succeeded in obtain optical CW lasing from a quasi-2D perovskite film, which will be important for the realization of electrically pumped perovskite semiconductor laser diodes.

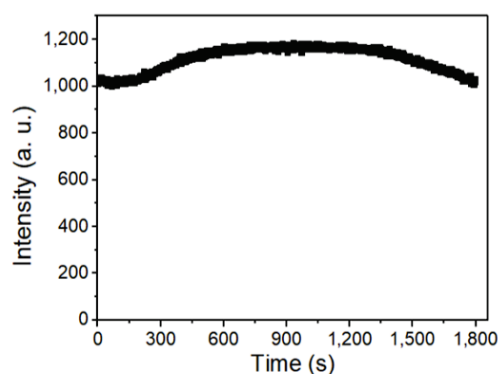


Figure 2. Optical CW lasing from a quasi-2D perovskite film. The laser intensity remain constant over 1,800 s in air at room temperature. Figure reprinted by permission from Springer Nature: Nature, 585, 53 (2020) (ref. 10).

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