Reducing Architecture Limitations for Efficient Blue Perovskite Light-Emitting Diodes

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Light-emitting diodes utilizing perovskite nanocrystals have generated strong interest in the past several years, with green and red devices showing high efficiencies. Blue devices, however, have lagged significantly behind. Here, it is shown that the device architecture plays a key role in this lag and that NiO_x, a transport layer in one of the highest efficiency devices to date, causes a significant reduction in perovskite luminescence lifetime. An alternate transport layer structure which maintains robust nanocrystal emission is proposed. Devices with this architecture show external quantum efficiencies of 0.50% at 469 nm, seven times higher than state-of-the-art devices at that wavelength. Finally, it is demonstrated that this architecture enables efficient devices across the entire blue-green portion of the spectrum. The improvements demonstrated here open the door to efficient blue perovskite light-emitting diodes.

Inorganic–organic perovskites have exploded in interest over the last several years, due to extremely strong photovoltaic performance.[1,2] The long diffusion lengths[3] and low trap densities[4] that drive this performance also mark these materials as strong candidates for light emitting diodes (LEDs).[5,6] Recent work has shown that green LEDs fabricated from these materials can reach external quantum efficiencies (EQEs) as high as 9.3%[7] and current efficiencies of 42.9 cd A⁻¹.[8]

Significant recent attention has turned toward high stability all-inorganic perovskite materials, with nanocrystals a particular interest. Following the development of a facile synthesis by Protesescu et al.,[9] interest in cesium-based lead halide perovskites has exploded due to their high photoluminescence quantum yields[9] and wide variety of applications. After an initial publication by Song et al. showed modest efficiencies around 0.1%,[10] work from several groups have demonstrated green LEDs with quantum efficiencies greater than 1%,[11–13] with the highest EQE of 8.73%[13] and brightness over 15 000 cd m⁻².[11] Similarly, red devices based on cesium lead iodide nanocrystals have shown high performances with quantum efficiencies over 5%.[14,15]

Despite finding some success in organic–inorganic perovskites, with EQEs up to 1.38%,[16,17] and 2D nanoplatelet perovskites,[18,19] inorganic blue devices have consistently lagged behind the more robust green and red ones.[15] Song et al. demonstrated a quantum efficiency of 0.07% with a brightness as high as 742 cd m⁻² with a 455 nm emission peak.[10] Pan et al. reported efficiencies of 1.9% as blue as 490 nm.[12] Recently, Yao et al. demonstrated a bright blue device based on a nickel oxide (NiO_x) hole-transport layer (HTL) and clever solvent engineering with a peak efficiency of 0.07%.[20] In order for perovskite LEDs to become commercially relevant, a solution to these low quantum efficiencies must be found.

In this work, we synthesize CsPbBr_xCl_{3-x} nanocrystals and demonstrate that their emission efficiency and lifetime are significantly impaired when used with HTLs such as NiO_x. By developing a device architecture that does not affect the emission of the nanocrystals, we are able to increase device performance to a maximum EQE of 0.50% and a brightness of 111 cd m⁻² at an emission wavelength of 469 nm. Finally, we demonstrate that these device improvements can be beneficial across the blue-green visible spectrum, with bright, efficient devices spanning from 511 to 469 nm.

We synthesize CsPbBr_xCl_{3-x} nanocrystals following the Protesescu et al. method[9] but at lower temperature to favor an asymmetric crystal growth in order to achieve slight quantum confinement.[23] The yielded nanocrystals are ≈20 nm in the lateral dimension and 5 nm thick. Figure 1b. The absorption and emission properties are presented in Figure 1c, demonstrating a narrow emission of 23 nm full width at half maximum (FWHM). These nanocrystals were robust to purification process by antisolvant (ethyl acetate) washing, and the washing was found to preserve their exciton confinement and emission but enable better charge injection.

The lagging blue device efficiencies of these materials, coupled with their relatively strong photoluminescence quantum yield (PLQY),[9] led us to suspect the device environment was playing a crucial role, especially in these thin nanocrystal layers where the emission layer is near to the interface. Therefore, we turned our focus to the surrounding layers, with a particular eye toward the HTL. In order to judge the effect of the local environment, we monitored the transient decay of a thin film of nanocrystals as a function of underlying layer. All data were measured in air with 379 nm excitation using a Hamamatsu streak camera integrated across the emission wavelength of the nanocrystals.

In Figure 2a, we compare the transient photoluminescence of nanocrystals spincast on top of glass (red) and NiO_x (orange)
in the first nanosecond after excitation. A clear decrease in lifetime is observed in the presence of NiO$_x$, which, when combined with the strong reduction in photoluminescence (see the Supporting Information), indicates the appearance of a nonradiative decay channel, possibly decaying through defect states in the NiO$_x$ or via a charge transfer process.

Thus, in order to obtain optimal emission efficiencies from the nanocrystals, it is necessary to find an HTL which does not introduce any nonradiative decay channels.

To improve the emission from the device, we turn to an HTL constructed of a bilayer of poly(9,9-dioctylfluorenyl-2,7-diyli)-co-(4,4’-(N-(4-sec-butylphenyl) diphenylamine) (TFB) and Nafion perfluorinated ionomer (PFI). TFB, an electron-blocking, hole-transport polymer with a high hole mobility of 0.01 cm$^2$ (Vs)$^{-1}$,[26] has been shown to be successful as an HTL in Cs-based perovskite LEDs.[15] PFI has been used successfully as part of a buffer hole injection layer leading to high brightness devices.[22,27] The strong surface dipole induced by PFI leads to a band bending of the underneath HTL layer to a higher work function, favorable for hole injection, while the isolation of the perovskite layers helps to reduce exciton quenching. Thus, we hoped that the combination of the two materials could lead to high performance blue devices.

Unfortunately for our transient photoluminescence (PL) study, the luminescence of TFB overlaps that of the nanocrystals, so in order to better understand their dynamics we first had to subtract the TFB-only emission from the samples. The details of this subtraction can be found in the Supporting Information. The final subtracted data are plotted in Figure 2b, blue. We observe that the transient decay is virtually identical to the emission from glass, demonstrating that the nanocrystals are not significantly perturbed by the presence of the HTL, and thus this HTL could substantially improve the emission from the nanocrystals relative to current HTLs. This improvement is further reflected in the increased steady state emission from the nanocrystals as compared to a NiO$_x$ underlayer, see the Supporting Information.

To more clearly quantify the benefits of this HTL switch, we fabricate devices utilizing both NiO$_x$ and TFB/PFI as the HTL, following the device structures in Figure 1e,f. Indium tin oxide (ITO)-coated glass is cleaned via solvent washing and plasma cleaning immediately before sequential spincoating of the HTL layers, either poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS), TFB, and PFI, or the NiO$_x$ precursor (followed by heating to form NiO$_x$). We found the PFI layer to be crucial to maintaining nanocrystal emission; without it, electroluminescence (EL) from mostly TFB
is observed (see the Supporting Information), agreeing with previous reports of improved film quality on top of PFI with low surface energy.\[21\] The nanocrystals are then spuncast from octane followed by transfer to a thermal evaporator, where 40 nm of 1,3,5-tris(1-phenyl-1H-benzimidazol-2-yl)benzene (TPBi) is evaporated, followed by LiF/Al to form the top contact and pattern the device with a diameter of 2 mm. All device fabrication is performed inside a glovebox; all device testing is done on unpackaged devices in air.

After device fabrication, we observe clear electroluminescence from the perovskite nanocrystal layer, Figure 3a, in both structures. The electroluminescence spectra from the two devices are nearly identical, with a peak of 469 nm and a FWHM of 24 nm for the NiO\(_x\) and 25 nm for the TFB/PFI. The emission is unchanged as a function of applied voltage, see the Supporting Information.

In Figure 3b,c we present the electrical characteristics of the devices. The NiO\(_x\) device, a much more conductive structure, demonstrates a low turn-on voltage and high brightness, but is limited by high dark current and the nonradiative recombination of the nanocrystals discussed previously, leading to a maximum EQE of 0.03\% in our measurements. This is similar to the 0.07\% measured by Yao et al.[20] and Song et al.[10] The TFB/PFI device, in contrast, demonstrates a higher turn-on voltage but a much lower dark current. This dark current reduction likely results from better film formation and reduced pinholes, see Figure S8 in the Supporting Information. The EQE achieves a maximum 0.50\% before rolling off at higher current densities. This high quantum efficiency clearly demonstrates the value of TFB/PFI as an HTL and represents a new efficiency standard for blue inorganic perovskite nanocrystals.

This efficiency gain is likely an accumulation of several benefits in addition to the increased luminescence demonstrated in Figure 2. Devices with the HTL material poly(9-vinylcarbazole), which has a much lower hole mobility, show a maximum EQE of 0.063\%, indicating that the high hole mobility of TFB helps to balance the injected charges (Figure S4, Supporting Information). Further, a strong reduction in film roughness is observed moving from NiO\(_x\) to TFB/PFI, indicating a more uniform film with reduced pinholes (Figure S8, Supporting Information). The additive effects of these gains results in the high overall efficiency of the TFB/PFI device.

Finally, to demonstrate the universality of the TFB/PFI device structure, we tune the bromide to chloride ratio in order to adjust the emission wavelength as shown in Figure 4a, while keeping the device structure constant. The fabricated devices

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**Figure 2.** a) Time-resolved photoluminescence data show the clear emergence of a nonradiative channel in nanocrystals on top of NiO\(_x\) as compared with glass. Data taken from the integration of streak camera data. b) Nanocrystals on TFB/PFI demonstrates dynamics identical to those of nanocrystals on glass, enabling unaltered emission inside the device structure.

**Figure 3.** a) Electroluminescence, b) \(J–V–L\), and c) EQE curves for LEDs fabricated using 469 nm perovskite nanocrystals and either NiO\(_x\) (orange) or TFB/PFI (blue) as the HTL.
have emission wavelengths at 469, 481, 488, and 511 nm, with narrow FWHM. The current–voltage–luminescence (J–V–L) characteristics are similar for all devices, with relatively low dark currents and turn-on voltages that increase with increased bandgap. The EQEs for these devices are plotted in Figure 4c. There is a substantial increase in efficiency as the emission wavelength redshifts; indeed, a small 7 nm emission wavelength difference between the 481 and 488 nm device results in a threefold difference in maximum EQE.

As the energetics are shifted toward the green, we see less gain in quantum efficiency relative to literature. While the 469 nm device shows a strong efficiency enhancement with the HTL change, the bromide device (511 nm) peaks at 2.37% EQE and 3423 cd m$^{-2}$, on the order of other CsPbBr$_3$ devices recently published.[11] We hypothesize that the energetic requirements for lower bandgap nanocrystals are much less restrictive, and thus the benefits of the TFB/PFI structure fade as the emission peak redshifts and other structures provide an equally favorable environment. The full set of device parameters can be found in Table 1.

Though an important step forward, significant work remains to be done before these materials are commercially relevant. The main drawback of the blue nanocrystals is their low PLQY in thin films, which we measure at 9% for the 469 nm emission batch. Future work must focus on increasing this luminescence yield while maintaining the spectrally narrow emission, as well as continual improvements to the surrounding architecture of the device. In addition, these materials suffer from degradation and ion segregation[28] under continuous bias in air, see Figure S7 in the Supporting Information, that must be addressed before commercialization.

In this work, we have demonstrated and overcome one of the key efficiency barriers in blue perovskite nanocrystal LEDs: the architecture itself. We have shown that the HTL can induce nonradiative recombination of the emissive state, fundamentally limiting device performance. The introduction of a new HTL, TFB/PFI, that does not greatly influence the nanocrystals, provides a strong overall boost in efficiency, with values reaching as high as 0.50% EQE for 469 nm emitting devices. We further demonstrate that this structure provides strong benefits across the blue-green portion of the spectrum, opening the door for a variety of new applications.

**Experimental Section**

**Perovskite Nanocrystal Synthesis:** All synthetic materials were purchased from Sigma Aldrich and used as received unless otherwise mentioned.

### Table 1. Device parameters of cesium lead halide blue-green devices.

<table>
<thead>
<tr>
<th>Peak Emission</th>
<th>Maximum EQE [%]</th>
<th>Maximum brightness, [cd m$^{-2}$]</th>
<th>Maximum Lit. EQE$^a$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>469</td>
<td>0.50%</td>
<td>111</td>
<td>0.07%[10,26]</td>
</tr>
<tr>
<td>481</td>
<td>0.44%</td>
<td>212</td>
<td>0.07%[10,29]</td>
</tr>
<tr>
<td>488</td>
<td>1.41%</td>
<td>830</td>
<td>1.9%[12]</td>
</tr>
<tr>
<td>511</td>
<td>2.37%</td>
<td>3423</td>
<td>8.73%[13]</td>
</tr>
</tbody>
</table>

$^a$Approximately at the Emission Wavelength or Bluer.
noted. Cs$_2$CO$_3$ (0.814 g, purity 99.9%), octadecene (40 mL, purity 90%), and oleic acid (2.5 mL, purity 90%) were loaded into a 100 mL flask, dried under vacuum at 120 °C for 1 h, and then heated to 150 °C under stirring and N$_2$ protection, yielding a clear Cs-oleate precursor solution. The solution was cooled to room temperature for storage, and reheated to 100 °C under vacuum before use.

PbBr$_2$ (179 mg, 0.488 mmol, purity 98%), PbCl$_2$ (73.2 mg, 0.2632 mmol, purity 98%), octadecene (20 mL), oleylamine (2 mL, purity 98%), oleic acid (2 mL), and trioctylphosphine (2 mL, purity 97%) were loaded into 100 mL three-neck flask, dried under vacuum at 130 °C for 1 h, and then heated to 150 °C under stirring. The yielded clear solution was heated to 165 °C under N$_2$ protection. Then, 1.75 mL of preheated Cs-oleate precursors were swiftly injected into the above solution which turned to a yellow color immediately. After reacting for 5 min, and redispersed in 8 mL of octane or hexane. The solution was precipitated by a PTFE filter (0.2 μm) before use.

The solution was cooled to room temperature for storage, and reheated postexchanging by a solution of PbBr$_2$/oleic acid/oleylamine in octadecene. For the 511 nm emission device, only the PbBr$_2$ precursor was used to synthesize CsPbBr$_3$. To purify the nanocrystals, an equal volume of anhydrous ethyl acetate (purity 99.8%) was added to the above crude product to precipitate the nanocrystals. After centrifuging at 4000 rpm for 5 min, the precipitation was dissolved in 10 mL of anhydrous hexane (purity 95%). The nanocrystals were washed again by anhydrous ethyl acetate (volume ratio of ethyl acetate:hexane 3:1), centrifuging at 7000 rpm for 5 min, and redispersed in 8 mL of octane or hexane. The solution was filtered by a PTFE filter (0.2 μm) before use.

**LED Fabrication:** Ni(NO$_3$)$_2$·6H$_2$O, Nafion perfluorinated resin solution 5 wt% in lower aliphatic alcohols and water (PFI), LiF (evaporation grade), and aluminum were purchased from Sigma Aldrich and used as received. ITO substrates, TPBl, and TFB were purchased from Luminescence Technology, Inc. and used as received. PEDOT:PSS was purchased from Heraeus (Clevios P VP AI 4083) and used as received.

For the NiO$_x$ precursor, 1.5 mL of each Ni(NO$_3$)$_2$·6H$_2$O and ethylene diamine were dissolved in ethylene glycol to obtain a blue colored complex. After stirring for 10 min, the solution was filtered by a 0.4 μm PVDF filter.

A 15 Ω ITO patterned glass was cleaned by sequential sonicating in Micron-90 detergent, 2x water, 2x acetone and then soaking in boiling isopropanol for 10 min. The films were dried under blowing air and treated with O$_2$ plasma at 200 W using 0.5 Torr O$_2$ gas for 5 min. On these clean ITO substrates, a thin layer of PEDOT:PSS (Clevios PVP AI 4083, filtered using 0.4 μm PVDF filter) was spun at 4000 rpm for 45 s (ramp = 2500 rpm s$^{-1}$), and annealed at 140 °C for 30 min in a nitrogen glovebox. After cooling, a TFB (4 mg mL$^{-1}$ in chlorobenzene) layer was spin coated at 3000 rpm for 45 s (2000 rpm s$^{-1}$ ramp), and annealed at 125 °C for 15 min. A thin layer of PFI (0.05 wt% in isopropanol) was then coated at 3000 rpm for 45 s and dried at 145 °C for 10 min. For NiO$_x$ thin films, the precursor solution was spun on plasma cleaned ITO at 2000 rpm for 90 s (2000 rpm s$^{-1}$), and annealed at 300 °C for 1 h in air. On top of these layers, perovskite nanocrystals in octane were coated using different spin conditions (see the Supporting Information for individual conditions) to achieve a uniform layer. These films were then taken in the evaporation chamber, where 40 nm TPBl, 1.1 nm LiF, and 60 nm Al were deposited at 6 × 10$^{-6}$ mbar at 2 Å s$^{-1}$, 0.2 Å, 3 Å s$^{-1}$, respectively. Devices were unpackaged and measured in air.

**Materials Characterization:** Morphologies of perovskite nanocrystals were characterized by TEM (JEOL 2100, 120 kV). UV–vis absorption spectra were recorded by a PerkinElmer Lambda 25, and the photoluminescence spectra were collected by an Ocean Optics spectrometer (QE Pro) pumped by a 365 nm LED source. The TFB mobility reported is from ref. [25], measured between 40 and 160 kV cm$^{-1}$ s$^{-1}$.

**Streak Camera:** Samples were excited by a 379 nm laser from a Hamamatsu (C10196) with an 81 ps pulse width. OD filters were used to reduce the excitation intensity. The excitation was incident at a 45° angle to the glass face. The PL was collected with a 25.4 mm focal length lens normal to the glass face. It was focused through a 400 nm longpass filter into an SP2150i spectrophotometer coupled to a Hamamatsu C10627 streak unit and C9300 digital camera. Data were integrated across the nanocrystal emission wavelength from 440 to 500 nm to obtain the curves presented in Figure 2.

**Device Characterization:** EL spectra were taken with an Ocean Optics QE Pro with 100 ms integration time with 1 mA sourced to the device from a Keithley 2400. Current-voltage and EQE characteristics were measured with an HP 4145A with a calibrated half inch ThorLabs photodetector physically pressed to the face of the device, removing the need for a geometric correction. The device (1 mm radius) was much smaller than the photodetector (9.7 mm). The photodetector was smaller than the glass slide (12.2 mm), which, combined with the black material construction of the EQE holder, blocks the collection of waveguided light, preventing overestimation of the EQE. Luminance was calculated from the J–V–L curves and the spectra of the device. The J–V–L curves were measured from low to high voltage. The reduction in performance at high current densities is likely a reflection of both roll-off and degradation while under test (see Figure S7 in the Supporting Information).

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**

M.G. and S.H. contributed equally to this work. S.H. synthesized the perovskite nanocrystals and performed materials characterization. M.G. fabricated and characterized the LEDs. D.N.C. performed materials characterization. All authors designed the experiments and contributed to the manuscript. The authors acknowledge the support of the Rowland Fellowship at the Rowland Institute at Harvard University.

**Conflict of Interest**

Harvard University is filing a patent based on this work.

**Keywords**

blue LEDs, device architecture, perovskite LEDs

Received: October 26, 2017
Revised: January 30, 2018
Published online:


