Quantum Dot Light-Emitting Diodes Based on Inorganic Perovskite Cesium Lead Halides (CsPbX$_3$)

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Semiconductor quantum dots (QDs) have attracted intensive studies in recent years, due to their unique optical properties, such as size-dependent emission wavelength, narrow emission spectrum, and high luminescent efficiency.$^{[1-3]}$ All of these attractive characteristics make QDs excellent candidates for the next-generation lighting and display, as well as optical communication technologies. Ever since the first CdSe QD-based light-emitting devices (QLEDs) were reported in 1994,$^{[4]}$ various QD candidates, including CdS, CdTe, InP@ZnSeS, and Cu-doped ZnInS, have been reported as potential emitting materials for QLEDs.$^{[5-11]}$ Obviously, the dominant materials for QLEDs investigated in the past 20 years have been limited to wurtzite or zinc blende Cd-based QDs.

In the last two years, the halide perovskite materials were demonstrated to be amazing semiconductors with high performance for not only solar cells but also for LEDs and lasers.$^{[12-16]}$ However, the stability issue has become the crucial problem of hybrid organic–inorganic halide perovskites (CH$_3$NH$_3$PbX$_3$, X = Cl, Br, and I).$^{[12-16]}$ Compared to hybrid organic–inorganic halides, all-inorganic perovskites exhibit higher stability and have huge potential in various optoelectronics.$^{[14]}$ To integrate high stability with quantum confinement effects, Kovalenko and co-workers fabricated the cesium lead halide (CsPbX$_3$, X = Cl, Br, and I) QDs, which exhibited outstanding optical properties, especially their tunable and high-quantum-yield photoluminescence (PL).$^{[17]}$ Inspired by recent lasing and LEDs of CH$_3$NH$_3$PbX$_3$, these all-inorganic perovskite QDs have huge potential to become a new class of emitting materials in future practical QLEDs. Up to now, QLEDs based on all-inorganic perovskite cesium lead halide nanocrystals have not been reported.

Here, for the first time, we report the QLEDs based on all-inorganic perovskite cesium lead halide (CsPbX$_3$, X = Cl, Br, I) nanocrystals. The high-quality CsPbX$_3$ QDs were synthesized through hot-injecting cesium stearate (CsSt) to PbBr$_2$ solution. The luminescence wavelength can be tuned by both the size of the QDs and varying the halide composite (Cl, Br, and I). The QDs can be easily dispersed in various nonpolar solvents (e.g., toluene, octane, and hexane) serving as ink for solution-based opto-electronic devices. The typical QLED device composed of ITO/PEDOT:PSS/PVK/QDs/TPBi/LiF/Al exhibits blue, green, and yellow electroluminescence (EL), which demonstrate that all-inorganic perovskite QDs have potential to become a new class of candidates for low-cost display, lighting, and optical communication applications.

These inorganic perovskite QDs were prepared via a typical synthesis method by hot-injecting cesium stearate into PbBr$_2$ solution at 170 °C. The involved ionic metathesis reaction takes only several seconds because the nucleation and growth kinetics are very fast. Electronic microscopy images of the perovskite QDs are presented in Figure 1. The monodisperse CsPbBr$_3$ QDs have an average diameter of 8 nm, with a cubic shape determined by the perovskite crystal structure (Figure 1a), which was clearly revealed by X-ray diffraction (XRD) patterns presented in Figure S1 (Supporting Information), and further confirmed by the lattice fringes of 0.58 nm as shown in high-resolution transmission electron microscopy (HRTEM) images (Figure 1b). The fast Fourier transformation pattern as inserted in Figure 1a and the HRTEM image in Figure 1b confirm the CsPbBr$_3$ QDs have a very good crystallinity, which is preferred for improving the luminescence efficiency and the LED device performance.

The enlarged HRTEM image (Figure 1c) and the high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image (Figure 2, Supporting Information) exhibit the single atom arrangement and the cubic crystal lattice of CsPbBr$_3$ QDs, which further confirm the high crystal quality. The atom configuration is in good accordance with the cubic CsPbBr$_3$ crystal structure. It is clearly seen in Figure 1d that the CsPbBr$_3$ QDs have the cubic shape, and the QDs are uniformly arranged on the carbon-coated Cu grid, exhibiting a strong tendency to form a film. The elemental mapping result (Figure 1e) exhibits that the Cs, Pb, and Br atoms are effectively and uniformly incorporated into the QDs.

These as-obtained CsPbBr$_3$ perovskite QDs exhibit the intrinsical quantum size effects. Their size can be controlled by the reaction temperature evidenced by TEM images (Figure S3, Supporting Information). The size of the QDs increases as the reaction temperature is increased. The typical PL peak of the CsPbBr$_3$ QDs prepared at 170 °C was located at 510 nm (Figure 2a), which shifted to longer or shorter wavelength sides when the size of QDs was increased or decreased, respectively.

Meanwhile, the PL properties can also be tuned by varying the anion element composition. When Cl anions were introduced into the reaction system, the CsPb(Cl/Br)$_3$ nanocrystals were prepared. The PL peak shifts to the higher energy direction as the Cl anion content is increased (Figure 2b). It is worth pointing out that the Cl anion addition will not influence the crystallinity,
monodispersity, and morphology of the QDs as proved in Figure S4 (Supporting Information). On the other hand, the I anions can shift the PL peak of CsPbBr$_3$ to the lower energy direction. From the PL spectra shown in Figure 2b, it can be clearly seen that the luminescence can be effectively tuned in the range from 420 to 585 nm by introducing the Cl and I anions. The dependence of PL spectra on the halide molar ratio is summarized in Table S1 (Supporting Information). The alloying QDs preserving the basic cubic CsPbBr$_3$ structures were revealed by XRD patterns (Figure S5, Supporting Information). The XRD pattern

Figure 1. a) TEM images and b) HRTEM images of monodisperse perovskite QDs. Inset of (a): selected area electron diffraction (SAED) pattern of CsPbBr$_3$ QDs. c) Enlarged HRTEM images of perovskite CsPbBr$_3$ QDs and the corresponding cubic crystal structure. d) STEM images and e) elemental mappings of CsPbBr$_3$ QDs.
features have no obvious change, with slightly changed peak positions (the smaller Cl$^-$ ions lead to a shift of the diffraction peaks toward the large angle direction, while the larger I$^-$ ions result in a shift toward the small angle direction). The corresponding QDs dispersed in toluene can emit light in the range from violet to orange under 365 nm light excitation as shown in Figure 2c. Besides the tunable emission color, their quantum yields are very high in the range of 60%–90%, especially the CsPbBr$_3$ QDs-assembled thin films with a PL quantum yield of >85%.

The synthesis of perovskite QDs was conducted with oleylamine (OAm) and oleic acid (OA) as surfactants. Therefore, the carboxy and amine groups in OA and OAm were adsorbed or grafted onto the surface of the QDs during the reaction. These surface alkyl groups facilitate the QDs to disperse in various organic media as inks (Figure 2c). The as-synthesized all-inorganic QDs can be stored for more than two months, exhibiting higher stability in contrast to organic–inorganic hybrid CH$_3$NH$_3$PbBr$_3$ perovskite nanocrystals (Figure S6, Supporting Information). In a word, these all-inorganic perovskite QDs, exhibiting a single-crystal structure, good dispersity, and high ink stability, are suitable for low-cost, solution-processed, and flexible optoelectronics.$^{[20–22]}$ Associated with the high PL efficiency and tunable light emission that cover the whole visible wavelength range, the cesium lead halide perovskite QDs have huge potential in light-emitting diodes.

The typical as-prepared QLED device (Figure 3a,b) consists of multiple layers in the following order: indium tin oxide (ITO), poly(ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS), polyvinylcarbazole (PVK), tris(8-hydroxyquinoline)aluminum (Alq3), and rubrene (RUB). A cross-sectional TEM image of the multiple layers is shown in Figure 3b, with distinct contrast. The flat-band energy levels are shown in Figure 3c.
(PEDOT:PSS, 40 nm), poly(9-vinlycarbazole) (PVK, 10 nm), perovskite QDs (10 nm), TPBi (40 nm), and LiF/Al (1/100 nm). Figure 3c shows a schematic illustration of the flat-band energy level diagram of the layers. Thin films of TPBi are employed as electron-transporting layers. The PVK is used as hole-transporting and electron blocking layers. The PVK can reduce the hole injection barrier, block the electron in the active layer, and hence allow the holes and electrons to effectively recombine in the QD emitting layers.

The current density–luminance–voltage ($J–L–V$) characteristic of the QLEDs based on the typical green CsPbBr$_3$ QDs is presented in Figure 4a. The turn-on voltages (calculated with a luminance of 1 cd m$^{-2}$) required for the QLED device are about 4.2 V. The luminance increases as the voltage is increased, which achieves the maximum value of 946 cd m$^{-2}$ under the applied voltage of 8.8 V. The normalized EL spectrum of the QLEDs is shown in Figure 4b. The device gives a very narrow EL, which is solely attributed to the band-edge emission of QDs with a slightly redshifted emission from the PL spectrum taken in the QD colloid solution. Excitingly, no any notable parasitic emissions originated from the charge transport layer (i.e., TPBi or PVK) can be observed in the entire EL spectrum under varied voltages (Figure S7, Supporting Information). The devices emit bright and uniform green light from the whole pixel under a bias of 5 V as shown in the inset in Figure 4b.

The current efficiency and external quantum efficiency (EQE) as a function of the luminance for the typical green QLEDs are shown in Figure 4c. A maximum current efficiency of 0.43 cd A$^{-1}$ and the EQE of 0.12% are achieved at a luminance of 100 cd m$^{-2}$. The power efficiency curve is also shown in Figure 4d with a value of 0.14 lm W$^{-1}$. The blue and orange QLED devices can also be obtained by using the above structure, and the device performances are summarized in Table 1. In our blue, green, and orange LEDs using the structure of ITO/PEDOT:PSS/PVK/QDs/TPBi/LiF/Al, the luminances of 742 cd m$^{-2}$, 946 cd m$^{-2}$, and 528 cd m$^{-2}$, with external quantum efficiencies of 0.07%, 0.12%, and 0.09%, respectively, have been reached. The performance of these LEDs based on the all-inorganic perovskite QDs can be further optimized in the future by balancing the

Table 1. Characteristics of QDs and QLEDs. PL (photoluminescence), EL (electroluminescence), $V_{on}$ (turn-on voltage), L (Luminance), EQE (external quantum efficiency), CE (current efficiency), and PE (power efficiency).

<table>
<thead>
<tr>
<th>QD</th>
<th>PL $\lambda_{max}$ (FWHM)</th>
<th>EL $\lambda_{max}$ (FWHM)</th>
<th>$V_{on}$</th>
<th>Max. EQE</th>
<th>Max. CE</th>
<th>Max. PE</th>
<th>Max. L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blue</td>
<td>452 nm (23 nm)</td>
<td>455 nm (20 nm)</td>
<td>5.1 V</td>
<td>0.07%</td>
<td>0.14 cd A$^{-1}$</td>
<td>0.07 lm W$^{-1}$</td>
<td>742</td>
</tr>
<tr>
<td>Green</td>
<td>514 nm (29 nm)</td>
<td>516 nm (23 nm)</td>
<td>4.2 V</td>
<td>0.12%</td>
<td>0.43 cd A$^{-1}$</td>
<td>0.18 lm W$^{-1}$</td>
<td>946</td>
</tr>
<tr>
<td>Orange</td>
<td>583 nm (21 nm)</td>
<td>586 nm (23 nm)</td>
<td>4.6 V</td>
<td>0.09%</td>
<td>0.08 cd A$^{-1}$</td>
<td>0.06 lm W$^{-1}$</td>
<td>528</td>
</tr>
</tbody>
</table>
charge transporting, improving the PL efficiency, as well as by removing the surfactants. High crystal quality and high PL quantum yields guarantee that all-inorganic perovskite QDs are promising semiconductors, and have huge potential in other optoelectronic devices, such as monochromatic narrowband photodetectors, solar cells, and lasers.

The EL spectra can be readily tuned by substitution of Br ions with I ions or Cl ions (CsPb(Cl/Br)₃, CsPb(Br/I)₃) as reflected in the PL spectra (Figure 2). Figure 5a–c shows the photographs of the QLED devices fabricated on a 4 × 4 cm² substrate under operation. These devices can emit uniform and large-area blue, green, and orange light. The normalized EL spectra of blue, green, and orange QLEDs with emission peaks at 455, 516, and 586 nm are shown in Figure 5d, with the full width at half maximum (FWHM) smaller than 30 nm for all colors (Table 1). All devices exhibit very saturated and pure colors, as demonstrated by the Commission Internationale de l’Eclairage (CIE) chromaticity diagram shown in Figure 5e. Compared to the National Television System Committee (NTSC) standard color (stars), the blue, green, and orange QLEDs can cover the upper left part of the CIE diagram. Although the all-inorganic perovskite CsPbX₃ nanocrystals can show the bright emission with a wide color gamut, the pure CsPbI₃ or CsPb(Br/I)₃ with a high molar ratio of I ions is not stable for preparing QLED due to its metastable state in the cubic phase.²³,²⁴

In summary, we fabricated blue, green, and yellow QLEDs with sharp emissions (FWHM < 30 nm) based on all-inorganic perovskite CsPbX₃ QDs for the first time. The colored QLEDs can be tuned from blue to orange by changing the content and category of anions. In the blue, green, and orange LEDs with a stacking layered structure of ITO/PEDOT:PSS/PVK/QDs/TPBi/LiF/Al, we achieved luminances of 742 cd m⁻², 2400 cd m⁻², and 946 cd m⁻², with external quantum efficiencies of 0.07%, 0.12%, and 0.09%, respectively. The resultant QLEDs demonstrate that the all-inorganic perovskite CsPbX₃ QDs can grow as a new family of photovoltaic material with great potential in a wide variety of optoelectronics, such as lighting, displays, monochromatic narrowband photodetectors, solar cells, and lasers.

**Experimental Section**

**Synthesis of CsPbBr₃ QDs:** 15 mL of octadecene (ODE), 3 mL of OA, and PbBr₂ (0.2 g) were loaded into a 100 mL four-neck flask, degassed at 100 °C for 10 min, mixed at 100 °C for 30 min, and heated to 170 °C in 10 min under Ar flow. 0.55 mL of Cesium Stearate (CsSt) solution (0.15 m in ODE) was quickly injected. After 5 s, the reaction mixture was cooled by the ice-water bath. The resultant QDs were precipitated by 20 mL of acetone and separated via centrifugation. The separated QDs were dispersed in 8 mL of 1-octane serving as ink for solution process QLEDs active layer.

**Device Fabrication:** PEDOT:PSS solutions (Baytron P VPAl 4083, filtered through a 0.22 µm filter) were spin-coated onto the ITO-coated glass substrates at 4000 rpm for 60 s and baked at 140 °C for 15 min. The hole transporting and electron blocking layer were prepared by spin-coating PVK chlorobenzene solution (concentration: 6 mg mL⁻¹) at 4000 rpm for 1 min. Perovskite QDs were deposited by spin-coating at 2000 rpm for 60 s. TPBi (40 nm) and LiF/Al electrodes (1 nm/100 nm) were deposited using a thermal evaporation system through a shadow mask under a high vacuum of 2 × 10⁻⁴ Pa. The device active area was 4 mm² as defined by the overlapping area of the ITO and Al electrodes. The devices were encapsulated in the glove-box by a cover glass slide using curable resin.

**Characterization and Device Measurements:** One drop of as-synthesized perovskite QDs dispersion was diluted and dispersed onto a carbon-coated Cu grid, and hexane was allowed to evaporate at room temperature. TEM and HRTEM images and energy-dispersive X-ray spectroscopy were taken on a Tecnai G2 F30 S-TWIN and Titan TM G2 60-300 TEM instrument. The PL spectra of the QDs were obtained by using a Varian Cary Eclipse spectrometer. The EL spectra and luminance (L)–current (J)–voltage (V) characteristics were collected by using a Keithley 2400 source, a calibrated luminance meter, and a PR-705 SpectraScan spectrophotometer (Photo Research) in air and at room temperature.

**Supporting Information**

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