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DOI:

[10.1021/acsami.9b07818](https://doi.org/10.1021/acsami.9b07818)

Document Version

Accepted author manuscript

[Link to publication record in Manchester Research Explorer](#)

Citation for published version (APA):

Zheng, C., Bi, C., Huang, F., Binks, D., & Tian, J. (2019). Stable and strong emission CsPbBr₃ quantum dots by surface engineering for high performance optoelectronic films. *ACS Applied Materials and Interfaces*. <https://doi.org/10.1021/acsami.9b07818>

Published in:

ACS Applied Materials and Interfaces

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ACS Appl. Mater. Interfaces, **Just Accepted Manuscript** • DOI: 10.1021/acsami.9b07818 • Publication Date (Web): 25 Jun 2019Downloaded from <http://pubs.acs.org> on June 28, 2019**Just Accepted**

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Stable and strong emission CsPbBr₃ quantum dots by surface engineering for high performance optoelectronic films

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Abstract

We demonstrated a complete surface passivation of CsPbBr₃ quantum dots (QDs) by treatment with di-dodecyldimethylammonium bromide (DDAB) and sodium thiocyanate (NaSCN), resulting in dispersions with photostable photoluminescence of near-unity quantum yield (~100%) as well as high carrier mobility of QDs-film. Br⁻ from DDAB and SCN⁻ from NaSCN passivated the bromine vacancies of the QDs to reduce the surface defect density and increase the stability. The QDs-passivated maintained the original photoluminescence intensity under ultraviolet irradiation from a 150 W xenon lamp for one hour, while the PL intensity of QDs-control quickly dropped quickly to 20% of its initial value. The shorter DDA⁺ ligands also improved carrier transport in the QDs-passivated film, which was verified by conductivity and space charge limited current measurements. When used as the photo-emitting species in a solution-processed LED structure, the surface treatment increased the maximum

luminance from 550 cd.m⁻² to 1200 cd.m⁻², and reduced the turn-on voltage from 3.1 V to 2.8 V.

KEYWORDS:

Inorganic perovskite, quantum dots, passivation, surface engineering, optoelectronics.

1. Introduction

Cesium lead halide perovskite (CsPbX_3 where $X = \text{Cl, Br, I}$) quantum dots (QDs) have recently generated significant interest as active materials for optoelectronic devices such as solar cells¹, photodetectors², light-emitting diodes (LED) and displays³⁻⁶. This interest is motivated by their size-tunable band-gap⁷, narrow line-widths, color purity and remarkably high photoluminescence quantum yield (PLQY). Monodisperse CsPbX_3 QDs with high photoluminescence performance were first synthesized using hot injection⁸ and exhibited emission tunable across the whole visible region, with the PLQY of green emitting CsPbBr_3 QDs as high as 90%. Huang et al. also reported using temperature to control reprecipitation, thereby achieving QDs with a size-tunable bandgap and a PLQY up to 93%.⁹ In 2017, red emitting CsPbI_3 QDs with a PLQY of nearly 100% was synthesized by introducing trioctylphosphine- PbI_2 as the reactive precursor.¹⁰ Recently, blue emitting CsPbX_3 QDs with PLQY over 80% were obtained by using a core-shell structure or by copper doping via a hot injection process.^{11, 12}

However, the practical application of CsPbX_3 QDs is currently limited by a number of issues. Despite their high tolerance to defects, which has been attributed to their ionic nature and the orbital composition of the energy bands¹³, CsPbX_3 QDs can nevertheless still suffer from the non-negligible effects of defects, such as a reduced carrier transport rate and a decreased PLQY. Also, the long-chain ligands, such as oleylamine (OAm) and oleic acid (OA), typically used to passivate the QD surface also impede carrier mobility within QD films, resulting in reduced device performance. Finally, the performance of CsPbX_3 QDs can degrade significantly during processing to a thin film, or on exposure to UV light.¹⁴ However, both theoretical calculations¹⁵ and experimental studies¹⁶ have suggested that, with appropriate surface passivation, defect reduction and enhanced stability could be simultaneously achieved. It has been

reported the PLQY of the CsPbBr₃ QDs can be greatly improved by proper surface passivation, but the excessive amount of surfactant suppresses charge transport, resulting in a decrease in device performance. Usually, the passivation process with single surfactant cannot completely passivated the surface defects of QDs, therefore, the PLQY can hardly close to unity. In addition, the stability and film conductivity cannot get simultaneously improved by the passivation process with one type of surfactant. Liu et al.¹⁷ used PbO and NH₄Br instead of PbBr₂ to control the ratio of Pb and Br, passivated the surface defects and enhanced the device effect, but the PLQY was only 75%. Similarly, woo et al.¹⁸ used an inorganic halide to passivate CsPbBr₃, which improved its stability, but its PLQY was only 78%. How to synergize passivated QDs by two possess making their PLQY of CsPbBr₃ close to uniform while enhancing its stability and device performance is very urgent.

In this work, a surface engineering strategy was developed for CsPbBr₃ QDs to enhance both PLQY and photostability, as well as allowing the production of QDs films with improved carrier transport. Recent work has demonstrated that the defects affecting the luminescence properties of CsPbBr₃ arise from bromine vacancies¹⁵. Didodecyldimethylammonium bromide (DDAB) and sodium thiocyanate (NaSCN) were thus used in sequence to passivate the surface bromine vacancies of CsPbBr₃ QDs, as shown in **Figure 1a**. Due to the strong affinity between Pb²⁺ and Br⁻, Br⁻ from DDAB combines with Pb²⁺ to fill bromine vacancies on the QD surface. At same time, DDA⁺ replaces some of OA on the QD surface. DDA⁺ is shorter than OA ligand, and is thus less of an impediment to transport between QDs. A small amount of OA was added prior to the DDAB treatment in order to protonate the OAm, promoting its desorption from the surface of the QDs¹⁹. The subsequent NaSCN treatment allows SCN⁻ to further

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4 repair the bromine vacancies. The QDs before and after passivation were characterized
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6 by Fourier transform infrared (FTIR) spectroscopy, x-ray diffraction (XRD), x-ray
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8 photoelectron (XPS) spectroscopy and transmission electron microscopy (TEM). The
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10 effect of this passivation strategy on dispersions of the QDs was determined via
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12 absorbance and photoluminescence (PL) spectroscopies, PLQY, PL decay time and
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14 photostability measurements. In addition, films were prepared from the QDs to allow
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16 charge transport to be assessed. Lastly, LEDs were fabricated via solution-based
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18 methods, and the effect of passivation on device performance determined.
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Figure 1 (a) The surface passivation mechanism on CsPbBr₃ QDs; (b) FTIR transmission spectra and (c) X-ray diffraction pattern of QDs-control and QDs-passivated; The 1s core-level spectra for N of (d) QDs-control and (e) QDs-passivated.

2. Results and Discussion

Figure 1b shows the FTIR spectra of CsPbBr₃ QDs solutions before and after passivation (from here on described as QDs-control and QDs-passivated, respectively). The spectrum for QDs-control features distinct absorption bands at 2850 cm⁻¹ and 2920 cm⁻¹, which are due to the asymmetric stretching vibration of CH₂ and CH₃ groups, respectively, and are attributed to the OA and OAm ligands. There is a similar feature for QDs-passivated which is weaker, consistent with a reduced contribution from OA and OAm which is not offset by the addition of DDA⁺. The QDs-passivated sample also shows a strong absorption peak at 2340 cm⁻¹, which is only weakly present for QDs-control. Absorption at this spectral position is associated with C≡N and so its increase is consistent with the addition of SCN⁻ to the QD surface. The crystal structures of QDs-control and QDs-passivated were analyzed by XRD as shown in **Figure 1c**. The XRD patterns both show four main peaks at 14.8°, 21.0°, 30.2°, and 37.2°, corresponding to the (100), (110), (200), and (211) planes, respectively, of bulk perovskite (see PDF#54-0752 database).¹¹ This pattern is evident for both samples demonstrating that the crystal structure of the CsPbBr₃ QDs has not been not significantly affected by the passivation process. The intensity of the (110) peak is stronger after passivation process, which may indicate that defects are rich on the (110) crystal plane and are eliminated by the passivation process.

X-ray photoelectron spectroscopy (XPS) studies were undertaken to verify the composition of the QDs surface before and after passivation. The XPS spectra of QDs-

control and QDs-passivated indicate the presence of the constituent elements of CsPbBr₃, plus C, and O. (**Figure S1**). **Figure 1d** shows the 1s core level of N for QDs-control and has been fitted with a pair of components centered at 398.3 eV and 400.8 eV, corresponding to an amine group and a protonated amine group (i.e. -NH³⁺), respectively.^{19, 20} In contrast, the 1s core level of N for QDs-passivated, as shown **Figure 1e**, can be described by a single peak centered at 401.0 eV, attributed to the tert-ammonium cations from DDAB. This indicates that DDA⁺ has to a large degree replaced OAm and OA on the surface of QDs-passivated, consistent with the FTIR data.^{19, 21} The Pb/Br ratio was also calculated from the XPS data and was found to be 1:2.5 and 1:2.9 for QDs-control and QDs-passivated as shown in **Figure S1c**, respectively, indicating that the bromine deficiency has been significantly reduced by the passivation process as intended.

Figure 2 TEM images (20 nm scale bar) of **(a)** QDs-control and **(b)** QDs-passivated; inset: HRTEM images (5 nm scale bar); **(c)** Absorption and photoluminescence of QDs-control and QDs-passivated; **(d)** PLQY statistics of QDs-control and QDs-passivated samples; **(e)** Time-dependent PL intensity under UV light for QDs-control and QDs-passivated. Inset: schematic diagram of UV stability test.

Figure 2a-b show TEM images for QDs-control and QDs-passivated. Each of the nanocrystals observed has an approximately square cross-section and the linear size average and standard deviation, which was unchanged by passivation, was 7.7 nm and 1.6 nm, respectively; size histograms for both samples are given in the Supporting Information (**Figure S2**). The insets to **Figure 2a-b** are high-resolution TEM images showing a lattice spacing of ~ 0.58 nm, which corresponds to the (100) lattice face of the cubic perovskite crystal phase. The UV-visible absorption and PL spectra are shown in **Figure 2c**, the shape and spectral position of which are not significantly changed by the passivation process, although the PL FWHM is reduced from 23 nm to 20 nm. To the best of our knowledge, the half-width of 20 nm is narrow in the current research

field of CsPbBr₃, indicating a narrower size distribution. However, a significantly greater PL peak intensity following passivation can be observed, with the PLQY increasing from 73% to nearly 100%. **Figure 2d** shows the distribution of PLQY values measured for a number of QDs-control and QDs-passivated samples. The average value of the QDs-control PLQY was 73%, and the average PLQY of the QDs-passivated was as high as 99.2%, and had a standard deviation of 0.65%, which was significantly lower than that of the control (1.14%). The passivation process not only increased the average PLQY to a value not significantly less than unity but also reduced the variation between samples. A decrease in the PLQY of CsPbBr₃ QDs on exposure to UV light has been reported previously¹⁴ and so the photostability of both QDs-control and QDs-passivated was tested by illuminating samples with 150W xenon lamp for 1h. As shown in **Figure 2e**, the PL intensity of the QDs-control sample reduced to 20% of its initial value over this time, whilst that of the QDs-passivated sample was unchanged. The time-dependent PL spectra for QDs-control under UV illumination is displayed in **Figure S3a**. This enhanced photostability is attributed to the replacement of the OA and OAm ligands, which are known to detach from the QD surface under UV radiation¹⁴, with DDA⁺, which has a strong affinity for negatively charged surface sites. We also studied the stability of QDs against water and heat as shown in **Figure S3b-c**. The PL intensity of mixture solutions of water and QDs with a ratio of 1:2 after stored for different time have been carried out. As shown in **Figure S3b**, the QDs-passivated can maintain 80% value of initial PL intensity, while the PL intensity of the QDs-control diminishes sharply to 60% of initial value, indicating that passivation improved the water stability

of the QDs. To study the thermal stability, the QDs were deposited on the glass slides and then heated to different temperatures in an ambient atmosphere. It is found that the QDs-passivated can maintain 60% of initial PL intensity even at 200 °C. In contrast, the QDs-control is degraded after annealing at 200 °C and the PL strongly diminishes to nearly zero. It demonstrates the better thermal stability of the QDs-passivated, due to the steric hindrance of DDA⁺ on the surface of QDs. So, this passivation process has greatly improved UV, water and thermal stability of CsPbBr₃ QDs.

Figure 3a shows the PL decay transients for samples before and after passivation. Each transient can be well described by a triexponential decay function, and the parameters resulting of a fit of this function to the data is given in **Table S2**. The PL decay for the QDs-passivated is slower than that of QDs-control, with the amplitude-weighted average lifetime increasing from 9.4 ns to 17.5 ns; passivation of CsPbI₃ QDs by trioctylphosphine produced a similar relative reduction in the decay rate.¹⁰ A slower relaxation rate indicates a lower density of traps which can be used as local sites for non-radiative recombination²², and is consistent with the increase in PLQY, although a small number of views believe that shorter radiation lifetimes are more favorable.²³ A non-monoexponential PL decay transient even for samples with ~100% PLQY has been noted previously for methylammonium lead bromide perovskite QDs and explained by a shallow trapping-detrapping process that returns carriers to band edge states, from where they can still recombine radiatively.²⁴ In **Figure 3b** the absorbance spectrum is plotted on a logarithmic scale for QDs-control and QDs-passivated, which allows an Urbach tail to be seen for both at energies less than the band gap. The Urbach energy,

E_U , was found by fitting the following expression to this tail:

$$\alpha(E) = \alpha_0 \exp \left[\frac{E - E_0}{E_U} \right]. \quad (1)$$

where a smaller E_U indicates a lower trap density. This fit yielded E_U values of 21 meV and 29 meV for the QDs-passivated and QDs-control, respectively, again consistent with the passivation process reducing the number of traps.

Figure 3 (a) PL decay transients obtained at a wavelength of 512 nm for QDs-control and QDs-passivated; (b) absorbance spectra for both samples showing Urbach tails.

Figure 4. (a) Photograph of the PL obtained from QDs-control and QDs-passivated films; (b) I-V behavior for films of QDs-control and QDs-passivated. Inset: the structure of the device used for the I-V measurement. The space charge limited current response of (c) QDs-control and (d) QDs-passivated films. Inset: device structure for this measurement. (e) Luminance of the devices versus driving voltage; inset: a photograph of a QDs-passivated LED at 3.3 V. (f) Normalized EL spectra for a voltage of 3.8 V, and inset, CIE chromaticity diagram under an applied voltage of 3.8V of QDs-passivated light emitting diodes.

The PLQY of QDs film typically drops sharply compared to the same QDs in solution due to the replacement, during the process of film-forming, of the native long-chain organic ligands that passivate the surface well with others that better enable charge transport but cause the formation of nonradiative recombination centers.²² Such

increased nonradiative recombination, as evidenced by a reduced PLQY, will reduce the performance of optoelectronic devices based on QD films. As shown in **Figure 4a**, the QDs-passivated maintain a significantly higher PLQY (52%) than the QDs-control (35%) after formation into a film, and is attributed to the decrease of surface defects following passivation. Moreover the passivation process was also found to improve the conductivity of the films, as shown in **Figure 4b**. This is supported by the space charge limited current (SCLC) measurements displayed in **Figure 4c-d**, with the structure of the electron-only FTO/SnO₂/QDs/ZnO/Ag device used for this measurement shown as the inset. Three featured regions can be observed in SCLC curve. For low voltages, the I-V relationship is linear ($I \propto V$), i.e ohmic conduction. At high voltages, the response is quadratic ($I \propto V^2$) i.e. is in Child's regime. In between these is the trap-filled limit (TFL) region, where $I \propto V^{n>2}$, which corresponds to the saturation of the of available traps by injected carriers. The voltage at which this behavior begins (V_{TFL}) is proportional to the density of trap states.²⁵ Here, the V_{TFL} of the QDs-passivated device is only 0.15V, which is much lower than that of QDs-control (0.28V) and demonstrates the improved charge transport performance produced by the passivation. To further evaluate the effect of our passivation approach on device performance, LEDs constructed with a device structure of ITO/PEDOT:PSS/TPD/QDs/ZnO/Ag (see **Figure S4**) were fabricated using an all-solution process, the details of which are given in the Methods section. Whilst it is difficult to obtain high performance LED devices using the all-solution fabrication approach, comparison between devices nevertheless allows the effects of passivation to be assessed. The luminance-voltage characteristics

of the green-emitting LEDs are shown in **Figure 4e**. The turn on voltage of QDs-passivated LED device is 2.8 V, which is lower than that of QDs-control LED (3.1 V), indicating that more effective charge injection has been established for QDs-passivated device.²⁶ The luminance of the QDs-passivated LED reaches a maximum of 1200 cd/m² at 3.3 V, whilst for the control device the maximum luminance is only 550 cd/m² and this is achieved at the higher voltage of 3.5 V. A photograph is given in the inset of **Figure 4d** showing the bright green emission from the passivated LED. The electroluminescence (EL) spectra for both LEDs is shown in **Figure 4f**, with the passivated device exhibiting a somewhat smaller FWHM (21 nm) than the control device (23 nm). The position of the emission from the QDs-passivated LED on the Commission Internationale de l'Eclairage (CIE) chromaticity diagram is shown on the inset to **Figure 4f**. These results indicate the QDs-passivated can improved carrier transport and exhibit the potential for the practical application due to the shorter DDA⁺ ligands in the QDs-passivated film.

3. Conclusions

We have demonstrated a strategy for preparing stable and high PLQY CsPbBr₃ QDs as well as high performance optoelectronic QDs-films by passivation with DDAB and NaSCN. The surface defect density of the QDs was reduced by filling the bromine vacancies with Br⁻ from DDAB and SCN⁻ from NaSCN. The PLQY of the CsPbBr₃ QDs was thereby significantly improved from 73% to ~100%. In addition, some of the surface ligands (OA and OAm) were replaced with DDA⁺ during passivation process,

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4 due to the strong affinity between DDA^+ and negative surface sites. The QDs-
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6 passivated can maintain the original PL intensity under ultraviolet irradiation from a
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8 150 W xenon lamp for one hour, while the PL intensity of QDs-control decreases to 20%
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11 of its initial value. The shorter DDA^+ ligands also improved carrier transport in the
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13 QDs-passivated film, which was verified by conductivity and space charge limited
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15 current measurements. LED prepared by an all-solution process from the passivated
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17 QDS showed a bright green emission at 520 nm with lower turn on voltage of 2.8 V
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19 and higher a maximum luminance of 1200 cd/m^2 than those of the control LED.
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25 **Methods**

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27 ***Synthesis and purification.*** The CsPbBr_3 QDs were synthesized using the hot injection
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29 method first reported by Kovalenko et al.⁸ Cs_2CO_3 (0.2g) , ODE(15 mL) and OA(1.5
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31 mL) were dried in a 100 mL 3-neck flask for 1.5h at 120°C, and then the mixed liquid
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33 was kept at 70 °C under a N_2 atmosphere of before injection. PbBr_2 (0.138g) and ODE
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35 (20 mL) were dried under vacuum in a 100 mL 3-neck flask for 1.5h at 120 °C, and
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37 then 1.4 mL of OAm and 1.4 mL of OA were injected into the flask under a
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39 N_2 atmosphere . The solution was heated to 190°C when the PbBr_2 completely dissolved,
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41 1mL cesium precursor solution was injected into the PbBr_2 precursor quickly. The
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43 resulting solution was then immediately cooled using ice-water. The CsPbBr_3 QDs
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45 were separated by the addition of methyl acetate (at a solution/methyl acetate volume
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47 ratio of 1:3), before being centrifuged for 5 min at 8000 rpm; finally the precipitate was
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49 dispersed in hexane.
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56 ***Treatment of CsPbBr_3 QDs.*** 70 μL of OA was stirred together with 1 mL of the purified
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58 CsPbBr_3 QDs (26 mg mL^{-1}), then 70 μL DDAB toluene solution (0.1M) was added
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immediately. After 5 min, this mixture was centrifuged with MeOAc (at a 1:1 volume ratio) before being redissolved in hexane. For the thiocyanate treatment, sodium thiocyanate (NaSCN) was stirred with the purified CsPbBr₃ QDs (26 mg mL⁻¹) for 30 min. After treatment, the excessing sodium thiocyanate was removed using a PTFE syringe filter.

Fabrication of optoelectronic films and LEDs.

Films. To form a perovskite film, the CsPbBr₃ QDs and passivated CsPbBr₃ QDs (in hexane, 26 mg mL⁻¹) were deposited via spin-coating onto the ITO coated glass substrates at 2000 rpm for 45s and then baked at 60 °C for 10 min.

LEDs. The ITO coated glass substrate was sequentially cleansed using deionized water, acetone and ethanol. The hole injection layer was produced via spin-coating PEDOT:PSS onto the substrates using a speed of 4000 rpm for 60s followed by baking at 140 °C for 10 min. To add the TPD layer, poly-TPD solution (with chlorobenzene as solvent) was deposited by spin-coating at 2000 rpm for 45s and then annealed under N₂ at 110 °C for 25 min. The preparation of the perovskite layer is the same as that of the above film. The ZnO films was deposited by spin-coating for 45 s at 2000 rpm and then annealing at 60 °C for 10 min. The Ag electrode was deposited using a thermal evaporation system under a vacuum of 3×10⁻⁵ Pa. The active area of LED was 10 mm².

Material and device characterisation. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were both undertaken on a JEOL JEM-2010 microscope at an operating voltage of 200 kV. The absorption spectra were acquired

using a Shimadzu UV-3600 plus and Beituo DUV-18S2 spectrophotometers. Photoluminescence spectroscopy was undertaken with a Gangdong F-280 fluorescence spectrophotometer. PLQY of films and QDs were estimated with an integrating sphere. In the UV light stability test, the light source intensity was 150 W and the distance from the sample was 8 cm. PL decay transients were obtained using a HORIBA Fluorolog phosphorescence lifetime system with excitation by a diode laser emitting 45 ps pulses at a wavelength of 375 nm. X-ray diffraction (XRD) samples were prepared by dropping CsPbBr₃ onto the glass substrates. The XRD spectra were acquired using a MXP21VAHF X-ray diffractometer incorporating a Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) source. X-ray photoelectron spectra (XPS) was acquired using PHI 5000VersaProbe III. XPS samples were prepared by dropping CsPbBr₃ QDs onto Si wafers. The Pb/Br ratio was found from the XPS data by calculating the ratio of the fitted peak areas, and taking into account the element sensitivity factor. Fourier transform infrared spectra (FTIR) was obtained using a Nicolet iS50 FT-IR spectrometer. The luminance (L)-voltages (V) curves and electroluminescence spectra of the LEDs were tested using a PR-655 SpectraScan spectrophotometer.

Supporting Information. The experimental Methods, XPS of QDs-control and QDs-passivated samples (Figure S1), Size distribution histogram for QDs-control and QDs-passivated samples (Figure S2), Water and thermal stability for QDs-control and QDs-passivated samples (Figure S3), Structure diagram for light emitting diodes. (Figure S4), parameters derived from the time-resolved PL decays of QDs-control and QDs-passivated samples. (Table S1).

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Acknowledgements

This work was supported by the National Science Foundation of China (51961135107, 51774034 and 51772026), Beijing Natural Science Foundation (2182039), National Key Research and Development Program of China (2017YFE0119700).

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