PbS Capped CsPbI₃ Nanocrystals for Efficient and Stable Light-Emitting Devices Using $p-i-n$ Structures

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ABSTRACT: Cesium lead halide perovskite nanocrystals (NCs) have unique optical properties such as high color purity and high photoluminescence (PL) efficiency. However, the external quantum efficiency (EQE) of the corresponding light-emitting diodes (LEDs) is low, primarily as a result of the NC surface defects. Here, we report a method to reduce the surface defects by capping CsPbI₃ NCs with PbS. This passivation significantly enhanced the PL efficiency, reduced the Stokes shift, narrowed the PL bandwidth, and increased the stability of CsPbI₃ NCs. At the same time, CsPbI₃ NC films switched from n-type behavior to nearly ambipolar by PbS capping, which allowed us to fabricate electroluminescence LEDs using $p-i-n$ structures. The thus-fabricated LEDs exhibited dramatically improved storage and operation stability, and an EQE of 11.8%. These results suggest that, with a suitable surface passivation strategy, the perovskite NCs are promising for next-generation LED and display applications.

Lead halide perovskite nanocrystals (NCs) are promising for next-generation light-emitting diodes (LEDs) because of their high photoluminescence quantum yield (PL QY), narrow emission bandwidth, and wide color gamut. The LED’s external quantum efficiency (EQE) has risen quickly from <1% to over 10% thanks to the surface ligand density control, interface engineering, and other treatments. The triple-ligand surface engineering strategy boosted the CsPbBr₃ NC ink’s stability and the LED’s EQE to 11.6%, which takes advantage of the ionic nature of perovskite NCs as it is easy for them to lose their surface ligands, revealing the important role of the NC surface.

On the other hand, the poor device stability still greatly impedes their practical applications. The rapid decomposition of perovskites in air limits the device storage and working lifetimes; their ion migration along crystal boundaries under bias can induce degradation and defects for nonradiative recombination, and thus harms the device operational stability. Nowadays, several groups have improved the perovskite NC’s stability using polyhedral oligomeric silsesquioxane, silica, and polymers but at the expense of their semiconducting property, making them not suitable for active optoelectronic devices. Thus, it is urgent to find a way to stabilize the crystal surface and prevent ion migration without damaging the semiconductor property of perovskite NC films.

Epitaxial solution growth has shown great potential in colloidal chemistry to obtain core/shell structures to passivate the unsaturated core surface sites, to reduce nonrecombination of photoexcited carriers, to optimize the semiconductor property, or to improve the material environmental stability. However, to the best of our knowledge, there is no example showing successful epitaxial growth of one semiconductor on the surface of perovskite NCs. Typically, the lattice mismatch between two different materials should be less than 15% for successful epitaxial growth. Sargent and co-workers demonstrated that perovskites and PbS can exhibit coherence in their lattice fringes due to their minimal lattice mismatch (<5%), pointing out a great possibility in obtaining high-quality perovskite/PbS nanostructures.

Studies have shown that the synthesis of lead halide perovskite NCs occurs at room temperature because of their ion nature, and the growth of perovskite on PbS is also feasible at room temperature. In comparison, the synthesis...
of covalent PbS NCs however needs high temperatures. We hypothesize that it may be possible to obtain PbS capped CsPbI3 NCs when CsPbI3 NCs are grown in a solution with ultrasmall PbS clusters available, through attaching these PbS clusters to the CsPbI3 NC surfaces. This idea was realized in this study.

Here, we report a strategy to simultaneously enhance the optical properties and stability of perovskite NCs without damaging their semiconducting properties by capping the CsPbI3 NCs with PbS. The surface defects of CsPbI3 NCs were well passivated with PbS capping, which significantly enhanced the PL efficiency, reduced the Stokes shift, narrowed the PL spectrum, and increased the stability. The introduction of PbS capping made the NC films switch from n-type behavior to nearly ambipolar which allowed us to fabricate electroluminescence (EL) LEDs using PbS as electron injecting layer. Nearly ambipolar which allowed us to fabricate electro-

Figure 1. (a) TEM and (b) HRTEM images of CsPbI3-0.1 NCs. (c) Proposed architecture of PbS capped CsPbI3 NCs. (d) Elemental mapping of CsPbI3-0.1 NCs. All scale bars represent 20 nm.

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the top of CsPbI₃ NCs. There would also be PbS attached on other sides of CsPbI₃ NCs with nonuniform thickness, leading to no particularly enhanced or decreased concentrations that follow the outline of the NC’s shell in the element mapping images. The X-ray photoelectron spectroscopy (XPS) measurements of PbS capped CsPbI₃ film at a different depth (Figure S4) further demonstrate the difference between the composition of the core and the composition of the shell: a ∼65% decrease in the S content was observed after removing a top layer by etching. There is no peak shift or shape change in the S 2p XPS spectra before and after etching, indicating the same chemical environment around S atoms. Thus, we conclude that S exists on the CsPbI₃ NC surface.

Now we have demonstrated that there is PbS in the final products from element mapping, and have proven that PbS is located on the CsPbI₃ NC surface. Since epitaxial growth is known to modify the NC surface and passivate defects, we used a series of optical property characterization to further confirm the successful capping of CsPbI₃ NCs with PbS. The transitions of absorption spectra (Figure 2a) for PbS capped CsPbI₃ perovskite NCs with different S:Pb ratios all located at 683 nm. In contrast, the PL peaks (Figure 2b) blue-shifted from 695 to 688 nm as the S:Pb ratio increased from 0 to 0.2. At the same time, the PL peak’s full-width at half-maximum (fwhm) decreased from 37 to 33 nm. The absorption and PL spectra of CsPbI₃-0.1 NCs are given as the inset of Figure 2b, showing the typical spectra of conventional perovskite NCs. Photos of CsPbI₃-0.1 NC toluene solution under daylight and 365 nm excited are given in Figure S5, revealing that the NC solution is perfectly transparent. The tail states in the absorption spectrum may originate from the small PbS particles.

The absolute PL QY and fwhm as functions of the S:Pb ratios are summarized in Figure 2c. The PL QY increased from 65% to 70% when the S:Pb ratio varied from 0 to 0.05, and then decreased to 66%, 65%, 50%, and 48% when the S:Pb ratio increased to 0.075, 0.1, 0.15, and 0.2, respectively. The CsPbI₃-0.1 NCs showed both high PL QY (65%) and superior
color purity (fwhm of 34 nm); thus, they were chosen for further research.

Time-resolved PL (TRPL) spectroscopy was carried out on pure and CsPbI3-0.1 NCs. It can be seen from Figure 2d that the PL average lifetime increases from 16.9 to 17.4 ns with the S:Pb ratio change from 0 to 0.1 (Table S1). As shown in the Figure 2d inset, the spontaneous radiative recombination between trap states generally leads to a lower energy emission compared with that from the band edge transition, and passivation of these trap states can blue-shift the PL peak.48 Additionally, the PL peak was narrowed, and the PL QY was increased by introducing PbS. We thus conclude that the NCs’ surface defects have been successfully passivated.

Figure 2e presents the X-ray diffraction (XRD) pattern of the CsPbI3-0.1 NC film. The diffraction peaks of both cubic CsPbI3 and PbS can be seen which indicates the existence of two individual phases. The chemical composition of the CsPbI3-0.1 NCs was analyzed via energy dispersive spectroscopy (EDS). As given in the Figure 2e inset, elements of Cs, Pb, I, and S are identified, and the elemental ratio of Cs:Pb:I:S is found to be 1:1.02:2.38:0.31. All elements were further confirmed with XPS (Figure 2f), and the results are consistent with EDS. No new peak appears in the FTIR spectra after PbS capping (Figure S6), indicating that CsPbI3 and CsPbI3-0.1 NCs have the same surface ligands, and thioacetamide does not serve as ligands here.

The Tauc plots and ultraviolet photoelectron spectroscopy (UPS) spectra of CsPbI3 and CsPbI3-0.1 NCs are given in Figure 3a. For pure CsPbI3 NCs, their Fermi level (−3.84 eV) and CBM (conduction band minimum, −3.78 eV) are close, clearly identifying their n-type behavior (Figure 3b). After PbS capping, the Fermi level shifts to −4.40 eV while the CBM and VBM (valence band maximum) values are unchanged, demonstrating the switch from n-type to nearly ambipolar (Figure S7). The surface chemistry of CsPbI3 NCs is different after PbS capping and thus changes the electronic property.49

The nearly ambipolar behavior of CsPbI3-0.1 NCs allowed us to build LEDs using p-i-n structures. The device energy band diagram for all functional layers is given in Figure 3b. A wide bandgap n-type ZnO NC film was chosen as both the

![Figure 3](https://example.com/figure3.png)

**Figure 3.** (a) Tauc plots of CsPbI3 and CsPbI3-0.1 NC films with their UPS spectra. (b) Device energy level diagram for all functional layers. (c) J–V–L curves with a working device photo. (d) EQE, \( \eta_D \), and \( \eta_L \) versus brightness. (e) Peak EQEs collected from 28 devices. (f) PL and EL spectra of the CsPbI3-0.1 NC LED; inset shows the corresponding CIE coordinates for the EL spectrum.
electron transport layer (ETL) and the hole blocking layer (HBL) because of its excellent optical transparency and deep lying VBM. A p-type 4,4′,4″-tris(carbazol-9-yl)triphenylamine (TCTA) film was chosen as the hole transport layer (HTL) and also the electron blocking layer (EBL) because of its suitable HOMO (highest occupied molecular orbital) and low electron affinity. The combination of ZnO and TCTA allows effective confinement of injected charge carriers in the emissive layer for radiative recombination. MoO3/Au and ITO/ZnO/polyethylenimine were used as the top and bottom electrodes, respectively, for their ohmic carrier injection property.

Figure 3c presents the J−V−L curves of the CsPbI3-0.1 NC LEDs and a working device with a 9 mm² emitting area. The devices had a low turn-on voltage of 1.9 V, which is close to the band gap energy of the emitters (1.78 eV), meaning that a highly efficient and barrier-free charge injection into the NC emitters was achieved. The luminance reached 1050 cd m⁻² at 6.7 V voltage and 397 mA cm⁻² current density. A peak EQE of 11.8% was achieved at 2.8 V (Figure 3d). The low-efficiency roll-off (7.6% of the EQE was preserved at 100 mA cm⁻²) indicates that the NCs kept a low charging degree even at high current densities. The peak current efficiency (ηₐ) and power efficiency (ηₑ) of the device were 0.81 cd A⁻¹ and 0.99 lm W⁻¹, respectively. Figure 3c shows an average peak EQE of 10% from 28 devices. CsPbI₃ NC LEDs with the same parameters were fabricated and compared (Figure S8).

Figure 3d displays normalized PL and EL spectra of a typical CsPbI₃-0.1 NC LED (Figure S9). Apparently the EL was from CsPbI₃ NCs without noticeable contribution from any charge transport materials. Therefore, the NCs were the exciton recombination centers for the device, and a balanced charge carrier transport was achieved. The symmetric emission corresponds to Commission Internationale de l’Eclairage (CIE) color coordinates of (0.73, 0.27).

The transformation from cubic to orthorhombic phase of CsPbI₃ NCs deteriorates their appealing semiconducting properties and greatly hinders their practical applications. Pure CsPbI₃ NCs showed poor solution stability, and turned from deep red to yellow in 3 days in air, similar to the published results. In comparison, both absorption and PL spectra of CsPbI₃-0.1 NC solution only experienced a slight red-shift after 20 days, while the solution color remained the same (deep red) (Figure 4a,b), representing a much better solution stability.

The phase stability of NC films is crucial for LED and solar cell applications. As shown in Figure 4c, XRD patterns of CsPbI₃-0.1 NCs demonstrate that the NCs remained in cubic phase even after 33 days of storage in ambient conditions, demonstrating the greatly enhanced phase stability by PbS capping. The storage stability of unencapsulated NC LEDs stored in nitrogen was also evaluated. Figure 4d shows that the EL intensity of CsPbI₃-0.1 LEDs is very stable with ignorable change after being stored for 35 days, while the EL intensity of pure CsPbI₃ LEDs decreased by 30−40% in 3 days. The significantly improved stability of the CsPbI₃-0.1 LEDs can be attributed to the PbS shell that stabilizes the crystallite surface. Stable CsPbI₃-0.1 NC films also empower improved device operation stability (Figure 4d inset, Figure S10). To avoid the impact from Joule heating, the devices were...
operated at a low voltage of 2.5 V. The EL intensity of pure CsPbI₃ LEDs dropped to 48% of their initial value in 600 s, while the EL intensity of CsPbI₃:0.1 LEDs showed a negligible change. Ion migration in perovskite films has been proven to induce degradation and generate nonradiative recombination sites in the emissive layer, which is responsible for the operation instability.²⁸ We thus conclude that PbS capping can help to stabilize the NC surface and impede ion migration of NC films (Figure S11). Improving charge injection through interface engineering to operate LEDs at lower voltages would further enhance the operation stability of the PbS capped CsPbI₃ NC devices.

In conclusion, we have shown that PbS capping can dramatically passivate the surface defects and enhance the optical and phase stability of CsPbI₃ NCs. Surface defect passivation induces enhanced PL efficiency, reduced Stokes shift, and narrowed PL spectrum. PbS capping also helps stabilize the NC surface and impede ion migration, thus significantly improving the device storage and operation stability. At the same time, CsPbI₃ NC films switched from n-type behavior to nearly ambipolar by PbS capping, which allowed us to make EL LEDs with p−i−n structures. As a result, the LEDs made from CsPbI₃:0.1 showed greatly improved performance including an EQE of 11.8%, and an average peak EQE of 10%. It is also worth investigating while the EL intensity of CsPbI₃-0.1 LEDs showed a negligible change.

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