Robustness to High Temperatures of Al₂O₃-Coated CsPbBr₃ Nanocrystal Thin Films with High-Photoluminescence Quantum Yield for Light Emission

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ABSTRACT: Lead-halide perovskite nanocrystals are a promising material in optical devices due to their high photoluminescence (PL) quantum yield, excellent color purity, and low stimulated emission threshold. However, one problem is the stability of the nanocrystal films under different environmental conditions and under high temperatures. The latter is particularly relevant for device fabrication if further processes that require elevated temperatures are needed after the deposition of the nanocrystal film. In this work, we study the impact of a thin oxide layer of Al₂O₃ on the light emission properties of thin nanocrystal films. We find that nanocrystals passivated with quaternary ammonium bromide ligands maintain their advantageous optical properties in alumina-coated films and do not suffer from degradation at temperatures up to 100 °C. This is manifested by conservation of the PL peak position and line width, PL decay dynamics, and low threshold for amplified spontaneous emission. The PL remains stable for up to 100 h at a temperature of 80 °C, and the ASE intensity decreases by less than 30% under constant pumping at high fluence for 1 h. Our approach outlines that the combination of tailored surface chemistry with additional protective coating of the nanocrystal film is a feasible approach to obtain stable emission at elevated temperatures and under extended operational time scales.

KEYWORDS: lead-halide perovskite, nanocrystals, quantum dots, photoluminescence, stability, amplified spontaneous emission, high temperature, atomic layer deposition, oxides

INTRODUCTION

Perovskite nanocrystals (NCs)¹⁻⁵ currently show record performance in various optoelectronic devices. Light-emitting diodes already present external quantum efficiencies exceeding 16% in the green spectral region,⁶ and very recently amplified spontaneous emission under continuous-wave excitation has been reported.⁷ Such optoelectronic performance has been reached after only a few years of intense research following the seminal work from Protesescu et al.⁸ Yet, a major hindrance of perovskite NCs is their limited stability,¹⁰⁻¹³ which leads to relatively short operational lifetimes of the respective devices notwithstanding the performance.¹⁴ In order to tackle this stability issue,¹ various computational studies have identified the NC surface as the main culprit.¹⁵⁻¹⁸ In addition, experimental studies on NCs synthesized via different methods¹⁹⁻²¹ have pointed out that the nature of the surface ligands plays a major role in the material stability. In this context, postsynthetic treatments are an interesting venue to increase the stability of perovskite NCs as well as to improve photoluminescence quantum yield (PLQY);²² such methods include ligand exchange procedures,²³ amine addition,²⁴ cross-linking,²⁵ MnCl₂ doping,²⁶ potassium incorporation,²⁷ and more. Atomic layer deposition (ALD) of a thin Al₂O₃ layer on NC films provides an additional pathway to improve stability and performance of thin films of NCs.²⁸⁻³３

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One important issue is the stability of the active layers under heating and at elevated temperatures in the range up to 100 °C. Such temperatures can occur during possible processing steps that follow the NC deposition, as, for example, resist baking in patterning by lithography or thermal evaporation of additional layers, but also during operation under high current density in LEDs or under harsh environmental conditions. The deposition of a thin oxide film, for example Al₂O₃, by ALD can be employed to improve the robustness of NC films to environmental conditions.

In this work, we investigate the impact of coating CsPbBr₃ NC films with a thin Al₂O₃ layer via ALD. We use CsPbBr₃ NCs passivated by didodecyl dimethylammonium bromide (DDAB) ligands (Figure 1) that have demonstrated excellent stability in solution and in films under ambient conditions. We obtain a PLQY of 75% from NC films prepared by spin-coating the colloidal solutions on soda lime glass substrates that is maintained after the deposition of the Al₂O₃ layer. We study the temperature stability of bare and alumina-coated NC films in heating and cooling cycles and find that the optical properties of Al₂O₃-coated films are not altered after a heating cycle up to 100 °C. Exceeding this temperature leads to irreversible reduction in emission intensity, which is analyzed in terms of PL decay lifetimes. With pulsed laser excitation, we evaluate the amplified spontaneous emission threshold and obtain a value of around 60 μJ/cm² for both bare and alumina-coated NC films. The PL of the films is stable for up to hundreds of hours at a temperature of 80 °C, and the ASE manifests only a moderate decrease in performance for optical pumping up to more than one hour. Such stability is of great advantage for reliable device operation and for the processing of devices that occurs after the deposition of the NC film.

Figure 1. (a) CsPbBr₃ NCs passivated with Cs-oleate ligands are obtained from synthesis and a ligand exchange to DDAB is performed in solution. (b) Thin films of NCs are fabricated by spin coating the ligand-exchanged solutions on glass substrates. (c) The films are coated with a thin Al₂O₃ layer via atomic layer deposition.

Figure 2. Bare and Al₂O₃-overcoated CsPbBr₃ DDAB-capped NC films. (a) Transmission electron microscopy image of the CsPbBr₃ NCs; scale bar is 100 nm. (b) Optical Absorption and PL spectra recorded from the NCs in solution. (c) Normalized PL emission of spin-coated CsPbBr₃ NC films, bare (red) and overcoated with a 13 nm thick layer of Al₂O₃ (blue). The inset shows an SEM image of the NC film demonstrating the homogeneity of the deposition. Scale bar is 1 μm. (d) PL decay traces of the bare and Al₂O₃-coated films.
Figure 3. PL emission during heating and cooling cycles of bare and Al2O3-coated CsPbBr3 NC films. (a,b) PL spectra recorded during heating the bare (a) and Al2O3-coated (b) films up 100 °C (373 K) and cooling back to room temperature (RT). (c,d) Normalized PL intensity obtained by integrating the area under the PL peak for bare (c) and Al2O3-coated (d) films. The PLQY of the bare film drops from 75% to 44% after one heating/cooling cycle, while that of the Al2O3-coated film fully recovers. Here, unity in PL intensity corresponds to PLQY of 75%. (e) PL intensity at 80 °C (353 K) recorded over time. The emission intensity remains above 80% for up to 100 h, and the PL decay traces recorded after 1 and 100 h (plotted in the inset) do not show any significant changes, confirming the stability of the optical properties.

## RESULTS AND DISCUSSION

Cs-oleate-capped CsPbBr3 NCs were prepared following our previously reported secondary amine-based synthesis procedure (see Materials and Methods for details). A post-synthesis ligand exchange was used to displace the native Cs-oleate ligands with DDAB (Figure 1). Contrary to the more commonly used primary alkyl ammonium or alkyl carboxylate ions, which can lose or acquire a proton, hence becoming charge neutral and detaching from the surface of the NCs, quaternary ammonium ions are more stable surface-passivating agents. The surface passivation with DDAB delivers NCs with near-unity PLQY in the solution phase without a ligand exchange was used to displace the native Cs-oleate ligands with DDAB (Figure 1).

Al2O3-coated films were treated with 200 cycles of thermal ALD that resulted in an alumina layer thickness of 13 nm. The excellent film uniformity can be appreciated in the confocal fluorescence microscopy image of the NC film in Figure S1a. Because of their brighter emission both in solution and in films, we focus on the following on the DDAB-passivated samples for the temperature and stability characterization.

Figure 2c shows the emission spectra of the pristine and Al2O3-coated NC films together with the PL decay traces. The PL peak position of the Al2O3-coated film is slightly blueshifted with respect to that of the bare NC film, which most likely is due to dielectric effects. The emission intensity is not affected by the alumina overcoating, and we obtained a PLQY of 75 ± 8% at room temperature from both bare and Al2O3-coated films. The PL decay of the bare and Al2O3-coated films is very similar, with average PL decay times of $\tau = 7.5$ ns for bare CsPbBr3 films and $\tau = 8$ ns for Al2O3-coated CsPbBr3 films. The minor change in average lifetime is mostly attributed to a small change in the dielectric environment caused by the alumina infilling of the voids. We conclude that the photophysical properties of the NC films is not affected by the coating with the Al2O3 layer. X-ray diffraction spectra recorded of bare and Al2O3-coated films confirm the structural stability (Figure S1b).

The temperature cycling in Figure 3b,d demonstrates the small changes in shape and line width. The Al2O3-coated film recovers the full PL intensity (PLQY of 75%) upon cooling back to room temperature, while the PLQY of the bare NC film is reduced after one heating/cooling cycle to 44 ± 4%. Humidity, ambient air, and temperature are known to influence the emission properties of perovskite NC films. The temperature cycling in Figure 3b,d demonstrates that the film coating with the alumina layer provides a sufficient protection that suppresses NC degradation for temperatures up to 100 °C. We attribute the main mechanism for the increased stability to the blocking of the desorption of the ligands that occurs at temperatures above 80 °C, which preserves the efficient surface passivation of the NCs. Similar data is shown for Cs-oleate-coated films in Figure S2, however...
in this case the PL intensity was already significantly reduced by the Al2O3 coating itself, and furthermore the alumina-coated films did not recover their full PL intensity after being cooled down to room temperature. Another important point is the stability over time at such elevated temperatures, which is reported in Figure 3e, where the PL intensity versus time under operation at a temperature of 80 °C is plotted for up to 100 h. We find a small decrease in PL intensity in the first few hours, and then the signal stabilizes at around 80% of its original intensity.

We have also tested the robustness of the NC film emission to temperatures exceeding 100 °C and found that the PL intensity is significantly reduced after heating up to 150 °C (423 K) for both bare and Al2O3-coated films, that is, it recovered only 60% and 50% of its original value, respectively, as shown in Figure 3e. We analyze the PL decay dynamics to gain deeper insight into this loss of emission intensity. The PL decay traces recorded over temperature displayed in Figure 4a,b show a maximum in PL lifetime around 100 °C (373 K). The decrease of the PL lifetime at temperatures higher than 100 °C can be attributed to fast nonradiative decay channels associated with heat-induced permanent defects, since in that case the PL is drastically and irreversibly reduced when the sample is cooled down to RT. This interpretation is corroborated by PL lifetimes associated with nonradiative defects, which are typically shorter (around 2–5 ns) than those of the radiative channels (around 10–15 ns).44

CsPbBr3 NC films are a very interesting material for amplified spontaneous emission (ASE)45–50 and lasing.51,52 Therefore, we investigated what effects the film protection by the alumina coating has on these properties. In Figure 5a,b, we report the ASE spectra of bare and Al2O3-coated DDAB-capped CsPbBr3 NC films (from a different synthetic batch as in Figures 2–4). In both cases, a clear ASE peak is observed with full width at half-maximum (fwhm) of ~4.5 nm for pump fluences exceeding 60 μJ/cm². Thus, the ASE threshold is not affected by the alumina coating of the NC film. Furthermore, the threshold of 60 μJ/cm² under femtosecond-excitation is comparable to other reports53 and roughly 1 order of magnitude higher compared to recently published results obtained from triple cation NCs that were engineered to optimize optical gain.54 ASE data of Cs-oleate-capped NC films are reported in Figure S4 and show comparable threshold

![Figure 4. (a,b) Contour plots of the PL decay traces versus temperature of bare and Al2O3-coated films in a heating cycle up to 150 °C (423 K), and the related average PL life times (c,d) obtained from fitting with three exponentials for both heating (red) and cooling (blue) cycles.](https://dx.doi.org/10.1021/acsanm.0c01525)
The ASE peak is centered at 527 nm and therefore slightly red-shifted compared to the photoluminescence (PL) peak, since ASE arises in a spectral range where the optical losses are minimized, that is, in the Urbach tail where self-absorption is reduced. The PL peak, measured in the direction normal to the substrate, is centered at 510 nm, consistent with our previous reports, while the PL peak recorded in the ASE configuration at grazing angles (see Materials and Methods) is red-shifted to 522 nm. Such red-shift can be attributed to self-absorption caused by the long trajectory of the emitted light within the NC film.

Stability tests of the ASE of the Al$_2$O$_3$-coated NC films over time at constant fluence of 430 $\mu$J/cm$^2$, thus around a factor of 7 above the threshold value, are shown in Figure 6 and revealed a decrease in ASE intensity of only 30% after 90 min (corresponding to $5.4 \times 10^6$ laser pulses). For comparison, the PL intensity of CsPbBr$_3$ NCs can show a decrease of 50% (or above) under constant optical excitation, while for PbBr$_2$-treated CsPbBr$_3$ NC films under femtosecond-optical pumping (at a fluence of 1.5 times the threshold value) the ASE demonstrated a similar decrease after $5 \times 10^6$ laser pulses. De Giorgi et al. estimated that ASE stability under nanosecond-excitation can be 4 orders of magnitude lower than that for femtosecond-pumping. In fact, the authors report a decrease of ASE intensity >50% after 3500 laser pulses employing nanosecond-excitation. Such results indicate that improvement in emission stability are required to achieve long operational lifetime, in particular in the pumping regime with longer laser pulses.

Motivated by the good stability of our NC films under high fluence pumping, we fabricated a distributed feedback (DFB) laser and plot the emission spectra in Figure 7a. We obtained lasing with a grating periodicity $d = 310$ nm under a detection angle of 10° with respect to the surface normal with a lasing threshold of 1 mJ/cm$^2$. At the threshold, multiple peaks can be observed, markedly at 526 and 529 nm. At higher pumping fluence, the peak at 529 nm takes over and dominates the spectrum with a narrow emission line width of $\sim 1.6$ nm. The observed mode spacing ($\Delta \lambda \sim 2.5$ nm) between the two lasing peaks could result from an additional outcoupling mechanism. In fact, DFB laser emission in the direction perpendicular to the lattice plane is obtained by a second order grating that acts as a loss channel. The emission was stable over time under lasing operation at a constant pumping fluence of 2.7 mJ/cm$^2$ (where a single laser peak was observed), and

![Figure 6. Emission spectra (a) and ASE peak intensity (b) of an Al$_2$O$_3$ coated NC film recorded over time under constant optical pumping with a fluence of 430 $\mu$J/cm$^2$.](image-url)
of our processing technique in the stabilization of light-emitting diodes or solar cells.

**MATERIALS AND METHODS**

**Chemicals.** Lead acetate trihydrate ((PbAc₂·3H₂O), 99.99%), cesium carbonate (Cs₂CO₃, reagent Plus, 99%), benzyol bromide (C₆H₅COBr, 97%), ethyl acetate (EA, 90%), toluene (anhydrous, 99.5%), didodecylmethylammonium bromide (DDDMAB), oleylamine (70%), octadecene (ODE, technical grade, 90%), and oleic acid (OA, 90%) were purchased from Sigma-Aldrich. Didodecyamine (DDDAm, 97%) was purchased from TCI. All chemicals were used without any further purification.

**Synthesis of Cs-Oleate-Capped CsPbBr₃ NCs.** Cs-oleate-capped CsPbBr₃ NCs were synthesized following our previously reported secondary amine-based synthesis approach. Briefly, lead(II) acetate trihydrate (76 mg), cesium carbonate (16 mg), and octadecene (10 mL) were combined in a 25 mL three-neck flask equipped with a thermocouple and a magnetic stirrer. The reaction mixture was degassed for 5 min at room temperature and then for 1 h at 115 °C. Then, a ligand mixture containing oleic acid (1.5 mL, previously degassed for an hour at 120 °C and stored in a glovebox) and didodecyamine (1.25 mmol, 443 mg) dissolved in 1 mL of anhydrous toluene was rapidly injected under nitrogen. After the complete dissolution of the metal precursors, the temperature was decreased to 70 °C and a solution of benzyol bromide (50 μL) in anhydrous toluene (500 μL) was swiftly injected. After 60 s, the reaction mixture was cooled down by using a water bath and was directly used for ligand exchange reactions.

**Ligand Exchange Reactions.** DDAB-capped CsPbBr₃ NCs were prepared following previously reported ligand exchange strategy. All ligand exchange reactions were performed under air. Briefly, the crude reaction mixture containing the CsPbBr₃ NCs (3 mL) was treated with an anhydrous toluene solution containing the DDAB salt (2 mL, 0.025 M) and the mixture was vigorously stirred for 1 min. Subsequently, the NCs were precipitated by the addition of 15 mL of ethyl acetate followed by centrifugation at 6000 rpm for 10 min. A second cycle of ligand exchange was carried out by redispersing the NCs in a toluene solution containing the DDAB salt (1 mL, 2 mM) and washing the NC dispersion with 6 mL of ethyl acetate and redispersion in toluene.

**Transmission Electron Microscopy (TEM).** Bright-field TEM images were acquired on samples prepared by drop-casting diluted colloidal solutions on carbon film-coated 200 mesh copper grids, using a JEOL-1100 microscope operating at an acceleration voltage of 100 kV.

**Film Preparation and Characterization.** CsPbBr₃ NC solutions were spin-coated on glass substrate at 2000 rpm for 1 min, which resulted in a film thickness of 50 ± 5 nm.

**Atomic Layer Deposition.** Atomic layer deposition was carried out in a Flexal ALD system from Oxford Instruments by using a thermal recipe with a stage temperature of 80 °C. Trimethylalumina (TMA) and H₂O were used as precursors. Before starting the alumina deposition, a preheating step of 300 s was performed. Each ALD cycle consisted of an H₂O/purge/TMA/purge with a pulse duration of 0.12/30/0.020/10 s, respectively. The process resulted in an alumina deposition rate of 0.065 nm/cycle.

**Optical Characterization.** PL measurements of the films were carried out with an Edinburgh Instruments fluorescence spectrometer (FLS920). The system included a xenon lamp with monochromator for steady-state PL excitation, a calibrated integrating sphere for PL quantum yield (PLQY) measurements and a time-correlated single-photon-counting unit coupled with a pulsed laser diode (λ = 405 nm, pulse width = 50 ps) for time-resolved PL studies.

**Heat and Cooling Experiments.** High-temperature heating cooling measurements were performed inside an Edinburgh fluorescence spectrometer (FLS920) with customized temperature-controlled holder from CaLCiTec srl. Measurements were performed on spin-coated and ALD-coated film on glass substrate of size 1.6 x 1.3 cm² in ambient atmospheric conditions by ramping the temperature from the peak intensity did not decrease significantly for 2.5 h (Figure 7b).

**CONCLUSIONS**

We have demonstrated that the coating of CsPbBr₃ NC films with a thin Al₂O₃ layer improved the robustness of the optical properties to elevated temperatures. Here, at temperatures up to 100 °C the film remained unaltered, demonstrated by full recovery of the high PLQY of 75% when cooling back to RT. Heating/cooling cycles to higher temperatures revealed that above 100 °C irreversible changes occur in the film that reduce the emission intensity, which is much more pronounced in bare NC films compared to the alumina-coated ones. Furthermore, also the threshold of ASE was unaffected by the alumina coating. The robustness of NC films up to 100 °C is highly favorable for technological applications, as many processing steps in device technology such as optical or electron-beam lithography and metal deposition rely on temperatures in this range. Also, the stability of optoelectronic devices under operation, heating of the active material can occur and there such robustness is paramount for stable performance. Therefore, we can foresee the exploitation...
Distributed Feedback Laser Fabrication. The lasing structures were prepared by drop-casting the CsPbBr₃ NC solution on a fused silica grating. The grating was bought from NIL Technology and presented linear grating intrusions within the fused silica substrate in an area of 200 µm × 400 µm.

Amplified Spontaneous Emission and Lasing Measurements. Films of CsPbBr₃ NCs were fabricated by drop-casting (with thickness of few µm) excited at a wavelength of λ = 405 nm using an amplified Ti:sapphire laser (Coherent Legend Elite seeded by a Ti:sapphire fs laser) with a 70 fs pulse (fwhm) and a repetition rate of 1 kHz. The ASE measurements were performed by focusing the excitation beam with a cylindrical lens onto the sample, thus obtaining a stripe-shaped beam profile. All ASE spectra were collected at 90° with respect to the excitation beam using an Ocean Optics HR4000 spectrometer coupled to an optical fiber. The lasing measurements were carried out using a spherical lens for focusing the beam and placing the DFB structure 80° with respect to the excitation beam (100° with respect to the collection optics).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsanm.0c01525.

Confocal fluorescence image of NC films, X-ray diffraction spectra of films before and after Al₂O₃ coating, PL decay fitting details and parameters, PL spectra of DDAB-capped NC films before and after heating to 150 °C, PL and ASE spectra of films consisting of Cs-oleate-capped NCs (PDF)

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