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Spray-Drying Polymer Encapsulation of CsPbBr₃ Perovskite Nanocrystals with Enhanced Photo-Stability for LED DownConverters

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ABSTRACT: Lead halide perovskite nanocrystals (LHP NCs) exhibit remarkable optical and optoelectronic properties but greatly suffer from poor stability in standard ambient and in-use conditions. These stability issues hinder their utilization in many technological applications and in their integration within industrial processes. Herein, we report a polymeric nano-encapsulation method of these NCs based on a spray-drying process, with the aim of using them as light down-converting materials in LED devices. CsPbBr₃ NCs were encapsulated in acrylate-based polymers to form NCs / polymer nano-composite beads, with an average diameter lower than 500 nm. Structural and optical characterizations demonstrated good preservation of the NC properties after the spray-drying despite quite harsh process conditions. Specific acrylate-based polymers were selected in order to match native surface ligands from our NCs. This was necessary to obtain an effective encapsulation within the beads. To evaluate the encapsulated NCs photo-stability under in-use conditions, bare NCs and encapsulated NCs were deposited on the chip of a blue LED down-converter to compare their luminescence stability. We observed that under continuous blue photon excitation, the NCs / polymer nano-composite beads exhibit a much better resistance to photobleaching compared to bare NCs.

INTRODUCTION

Colloidal lead halide perovskite semiconductor nanocrystals (LHP NCs) have attracted much interest since their first hot-injection synthesis reported in 2015.¹ LHP NCs exhibit remarkable optical properties: their photoluminescence quantum yield (PLQY) can reach near unity, they possess a narrow emission spectrum which is tunable over the visible spectrum, and have demonstrated great potential for unique photon sources.² Owing to their intrinsic defect tolerance and ease of synthesis, LHP NCs have been employed in many fields of applications, such as light-emitting diodes (LEDs),^{3,4,5} solar cells,^{6,7} cell imaging,^{8,9} single photon emitters,^{10,11} and security bar codes.^{12,13} However, LHP NCs suffer from poor stability due to their low formation energy and strong ionic nature.^{14,15} Particularly, the luminescent properties of LHP rapidly degrade in solid-state under ambient conditions, i.e. in presence of oxygen and moisture, or under in-use conditions with heat or light stress,^{16,17,18,19} limiting their potential integration in devices at the industrial scale.

Since their discovery, tremendous efforts have been made to stabilize the properties of LHP NCs. Various studies have been conducted on the chemical stabilization of the LHP NCs, by ligand engineering,^{20,21,22} or by synthezation of core/shell heterostructures.^{23,24} These routes effectively led to better stability in solution, but still lack of promising results in the solid-state. Different materials were also explored as host matrices to encapsulate and protect LHPs NCs from external stresses, such as polymers.^{5,9,25,26,27,28,29,30,31,32,33,34}, metal

oxides,^{35,36,37,38} metallic salt,³⁹ metal organic frameworks,^{12,40} or graphene/2D materials,^{41,42}. LHP NCs / polymers composite films were the first materials to be tested, thanks to the simplicity and the soft conditions of polymer processability which suite well to the poor stability of LHP NCs. For example, in 2016, Raja. *et al.* formed micron thick composite films by simply blending CsPbBr₃ NCs and high-molecular-weight polymers such as polystyrene and acrylate-based polymers.²⁵ More recently, Lu *et al.* used a hydrophobic fluoropolymer to form 100 nm thick composite films with the same blending method, reaching a high stability in water for temperature imaging in digital microfluidics.³⁴ *In situ* polymerization was also studied,^{27,28,30,33} for example Tong *et al.* developed an ultraviolet polymerization after a blade coating of a mixture of CsPbBr₃ NCs; using monomers as both ligands and solvent, the obtained films showed promising photostability against continuous illumination.³⁰

Even if remarkable stability improvements have been made in the past few years for composite NCs / polymeric films, these macroscopic encapsulation approaches are only tailored to a few applications, mainly for optoelectronic devices. Instead of embedding NCs in macroscopic matrices, another approach consists of forming micro- or nano-composite polymeric particles. These composite particles present several advantages ranging from their ability to be dispersed and incorporated in media or other matrices, simplified handling, and additional surface functionalization is possible. Until now, different methods have been developed to form polymeric beads with fluorescent NCs inside, including: swelling/shrinking

methods,^{9,43} suspension polymerization,^{44,45} electro-spray,⁴⁶ or microfluidic jet-mode breakup.⁴⁷ For LHP NCs, Wei *et al.* have formed CsPbBr₃ NCs / polystyrene nano- and micro-composite beads by a swelling/shrinking strategy with superior water-resistant properties. Similar approaches have also been developed for nanocomposite LHP NCs / polymers micro-composite fibers.^{29,31}

Despite these notable advancements, there is always a need for effective and scalable methods to produce LHP NCs / polymer nano-composite particles. Furthermore, a deeper study of their photo-stability is needed to evaluate their performance and determine their potential as light down-converting materials in LED applications. To achieve this objective whilst proposing a new approach for the fabrication of nano-composite particles with improved stability, we wanted to explore the utilization of a spray-drying method to encapsulate LHP NCs in polymeric beads. This process has been known since the late 19th century⁴⁸ and is currently a cost-effective, facile, and scalable process.⁴⁹ The spray-drying process is widely used in the pharmaceutical, flavor, and food industries. The adoption of this technique is widespread as it permits manufacturers to produce a dry powder from a solution of chemical components by atomization into small droplets dried in a hot zone to obtain solid beads.^{49,50} This technique can serve to simply dry active substances or to encapsulate target molecules, such as drug-loaded carrier systems.^{50,51,52} Because spray-drying is suited to sensitive components thanks to its fast drying step (few milliseconds), it seemed interesting to us to encapsulate LHP NCs with this process and measure the potential stability improvements. To the best of our knowledge, only one similar combination had been reported in 2006 by Chu *et al.*, who successfully incorporated CdTe quantum dots in bovine serum albumin for bio medical applications, but the final photo-stability of their micro-composite beads was not evaluated.⁵³

Herein, we report an effective encapsulation method based on a spray-drying process, to produce CsPbBr₃ NCs / polymers nano-composite beads. We employed acrylate-based polymers and managed to obtain beads within a fine range of drying temperatures. We performed morphological, structural, and optical characterization on the composite beads. The influence of the NCs surface ligands on the encapsulation was of paramount importance, since we show that only CsPbBr₃ NCs with short native ligands were properly encapsulated within the polymeric beads. Spray-dried CsPbBr₃ NCs conserved their initial structural properties while the PLQY was much better preserved at solid-state compare to films of bare NCs. The photo-stability of NCs / polymer nano-composite beads was studied using a LED down-converter device with “NCs on-chip” deposition. We measured an improved NCs photo-stability with the spray-drying encapsulation, resulting in a stable green emission that was recorded after 200 h of continuous photon excitation.

RESULTS AND DISCUSSION

Because NC surface ligands and polymer matrix interactions play an important role in NC dispersion,⁵⁴ two syntheses of CsPbBr₃ NCs with different surface ligands were studied to develop the spray-drying polymer encapsulation. First, CsPbBr₃ NCs with long ligands (CsPbBr₃-LL) were synthesized following a classical hot-injection synthesis based on the protocol developed by Protesescu *et al.*,¹ where oleic acid and oleylamine play the role of long alkyl chain stabilizers.

Second, CsPbBr₃ NCs with short ligands (CsPbBr₃-SL) were synthesized following a room-temperature synthesis based on the protocol developed by Akkerman *et al.*,⁷ with propionic acid and butylamine as stabilizers.

Figure 1. HAADF scanning transmission electron microscopy images of (a) CsPbBr₃-LL NCs and (b) CsPbBr₃-SL NCs. (c) Absorption (black line) and emission spectra (green line) of CsPbBr₃-LL NCs (top) and CsPbBr₃-SL NCs (bottom) in toluene solutions.

As shown in Figure 1a and 1b, CsPbBr₃-LL NCs exhibited a cubic shape with an average lateral dimension of 9.1 ± 1.3 nm according to HAADF-STEM images, whereas CsPbBr₃-SL NCs exhibited crystalline domains of 19.6 ± 6.1 nm in size, revealing higher size dispersity for the short ligand synthesis. Moreover, while CsPbBr₃-LL NCs were well separated from each other on the TEM grid due to the presence of long organic ligands, CsPbBr₃-SL NCs were agglomerated since short ligands cannot maintain a steric barrier between NCs. Analyses of high-resolution STEM images confirmed that both types of NCs crystallized in the orthorhombic crystalline structure of CsPbBr₃ perovskite (Figure S1 and S2). The optical properties of the NCs are shown in Figure 1c. The CsPbBr₃-SL NCs absorbance spectrum illustrates the presence of light scattering, a phenomenon mainly due to the poor colloidal stability of the NCs, since short ligands induced weaker steric barriers than long ligands.⁵⁵ This difference of colloidal stability was clearly identified by the turbidity of the suspension of CsPbBr₃-SL NCs after synthesis and purification (Figure S3). The photoluminescence (PL) spectra showed an emission peak centered at 517 and 520 nm for CsPbBr₃-LL and CsPbBr₃-SL NCs respectively, with a full width at half maximum (FWHM) of 18 and 22 nm, respectively. The absolute PLQY was measured at 70-80 % for CsPbBr₃-LL NCs and 60-70 % for CsPbBr₃-SL NCs, depending on the synthesis batch.

Figure 2 shows a sketch of the spray-drying process for nano-encapsulation of CsPbBr₃ NCs within polymeric beads. The initial solution feed was composed of CsPbBr₃ NCs and a specific formulation of polymer dissolved in toluene at 4 wt%. Toluene was used as the solvent because of its good compatibility with LHP NCs and its capability to dissolve many commercial hydrophobic polymers. The spray-drying process

Figure 2. Schematic illustration of the spray-drying process for the nano-encapsulation of CsPbBr₃ NCs in polymeric beads.

can be divided into three main steps. The first step involves the atomization of the solution feed into micrometric droplets. In the second step, these solvent droplets containing the solubilized polymeric chains and CsPbBr₃ NCs were pulled along the glass tube by a nitrogen flow and then dried in a hot zone heated by a tubular furnace in the range of 170–290 °C. At this stage, the solvent was quickly evaporated, and the polymer condensed into a spherical shape that encapsulated the NCs. In the last step, the resulting dried polymeric beads containing CsPbBr₃ NCs were collected on a filter. The encapsulation process is very rapid, taking less than 1 second between the first droplet formation and the first dried beads collected on the final filter. We measured a material yield around 50 %, corresponding to the weight ratio between the initial compounds (polymers + NCs) and the final beads weight collected on the filter. Most of the material loss was due to the dried polymer that remained stuck on the inner glass tube surface. This materials loss is intrinsic to the small-scale spray-drying setup used in this study, higher material yield is expected when using an industrial scale spray-dryer.

Different hydrophobic polymers were tested and each one was evaluated through three main criteria: to obtain solid polymeric beads, to retain the CsPbBr₃ NC photoluminescence properties, and to get an homogeneous NCs dispersion within the beads. In this work, we will only discuss the polymeric formulation with 50:50 in weight of poly(methyl methacrylate) (PMMA) and poly(butyl methacrylate-co-methyl methacrylate) (PBMA) as it led to the best results among the different formulations tested, mainly in terms of NCs dispersion within the polymeric matrix as it will be discussed below.

We first tested the spray-drying encapsulation of short ligand LHP NCs. Figure 3a shows a SEM image of typical PMMA:PBMA 50:50 w:w beads obtained by spray-drying encapsulation of CsPbBr₃-SL NCs with a heating temperature of 170 °C. The obtained polymeric particles presented a spherical shape. As shown in Figure 3b, the beads size distribution was found to be very wide, the particle size is in the range of roughly 40 nm – 2 µm, with an average diameter of ~430 nm, calculated from representative samples with a minimum of 500 beads. Most of the obtained polymeric beads

were smaller than 1 µm since 90 % of the beads had a diameter lower than 800 nm. It is well known that the size distribution mainly depends on the atomizer technology,⁵⁶ in this work we used an impactor nozzle atomizer type which generated droplets from 0.1 to 5 µm in diameter. This broad size distribution can be due to random formation of larger droplets, or to droplet fusion before the drying step.⁵⁷ Such high polydispersity and micrometric size objects can be a problem for further use in applications, such as device integration. Different subsequent sorting techniques have been studied, such as cyclone⁵⁸ or cascade impactor,⁵⁹ and could be used in the future to avoid the presence of large beads and to improve the size dispersity.

Figure 3c shows typical images under ambient light and UV excitation of the polymeric powder obtained by spray-drying. The tubular furnace temperature was one of the key parameters of the spray-drying encapsulation process. For a tubular furnace temperature at 130 °C or lower, no powder was collected but instead, a uniform film of polymer was formed on the filter. The solvent evaporation was certainly not complete ($T_{\text{eb}}(\text{toluene}) = 110$ °C) and led to an agglomeration of half-liquid half-solid polymers on the filter, which then dried slowly on the membrane to form a uniform film. Even if the tubular temperature was set to 130 °C, the temperature perceived by the droplets within the glass tube is approximately 50 °C lower than the target temperature. On the opposite side, for a tubular furnace temperature at 290 °C or higher, a uniform film of polymer was also formed onto the filter but not for the same reason. In this case the formation of the polymeric films was due to beads coalescence. Indeed, the acrylate-based polymers we used in this study have low glass-transition temperatures ($T_{\text{g,PMMA}} = 105$ °C; $T_{\text{g,PBMA}} = 52$ °C). When exposed to high temperatures, these thermoplastic polymers tend to become more viscous and lose their initial shapes. Figure 3d also shows the influence of the tubular furnace temperature on the final PLQY of composite beads containing CsPbBr₃-SL NCs. The final powder PLQY was 35 ± 1 % for a process temperature of 170 °C and dropped to 30 ± 1 % at 210 °C and 21 ± 1 % at 250 °C. This trend line is in good agreement with the poor stability of LHPs against thermal stresses,¹⁹ moreover, the PLQY drop might have been caused by ligand desorption during the spray-

Figure 3. PMMA:PBMA 50:50 w:w beads after 170°C spray-drying encapsulation of CsPbBr₃-SL NCs: (a) scanning electron microscopy image, (b) size distribution, (c) a picture of powder under ambient light (left) and 405 nm UV excitation (right), and (d) PLQY depending on the tubular furnace temperature, red cross indicates that no beads were obtained at this temperature.

drying process. PLQY variations compared to bare NCs are discussed below. Similar results on the morphology, size distribution and temperature dependency on PLQY were obtained for CsPbBr₃-LL NCs spray-drying encapsulation (Figure S4 and S5). The size distribution was very similar, showing that it is mostly polymer and process dependent. The PLQY of the spray-dried NCs with long ligands also decreased with process temperature increasing, however the loss was smaller compare to short ligands, probably because long ligands can desorb less easily.⁷

The NCs dispersion within the beads was further investigated by STEM analysis. HAADF STEM images clearly indicated that CsPbBr₃-LL NCs (Figure 4a) after spray-drying were located on the polymeric beads surface and were not encapsulated. To disperse the NCs within the matrix was the most complicated part of this work, indeed we did not succeed in properly encapsulating CsPbBr₃-LL NCs with any tested polymers as NCs were always found on the beads surface. We hypothesized that the interaction between acrylate polymeric chains and long ligands of CsPbBr₃-LL NCs (oleic acid and oleylamine) were not strong enough to prevent separation between the solidifying polymeric phase and the NCs during the solvent evaporation. The polarity difference between long alkyl nonpolar surface ligands of CsPbBr₃-LL and more polar acrylate polymers may explain their poor affinity.

For spray-dried CsPbBr₃-SL NCs, HAADF STEM images revealed that NCs were inside the polymeric beads (Figure 4b), which explicitly demonstrated the CsPbBr₃-SL NCs encapsulation with the spray-drying process. We believe that

in solution the affinity between CsPbBr₃-SL NCs and PMMA:PBMA is increased due to better interaction between ligands and polymeric chains, which consequently prevents any phase separation during the solvent evaporation and polymer solidification. In this case, NCs surface ligands and polymeric matrix had similarities in their chemical nature: propionic acid and butylamine for the NC surfaces; grafted butyl groups for the acrylate polymers. Raino *et al.* suggested in 2019 to improve the interaction between polymers and ligands by using grafted polymers with specific alkyl chains to match the surface chemistry of CsPbBr₃ NCs,³² which is in line with our observations in terms of NCs-polymers affinity.

To highlight the influence of the nano-encapsulation on the CsPbBr₃ NCs properties, PL, PLQY and XRD analyses were performed on spray-dried NCs with long and short ligands and were compared to corresponding bare CsPbBr₃ NCs in solution or in film. NC solutions were dispersed in toluene and NC films were made by drop casting NC solutions on a glass substrate under ambient conditions and allowed to completely dry before analysis. PL peaks of NC films with bare CsPbBr₃-LL and CsPbBr₃-SL NCs were respectively red-shifted by 9 nm and 10 nm compared to the PL peaks in solution (Figure 5c). An increase in FWHM of 6 nm and 8 nm is also observed, respectively. PL redshift and FWHM increase may be attributed to NCs aggregations and bulk-like contribution.⁶⁰ These observations indicated a partial degradation of the NCs PL properties in solid-state after deposition, which is one of the numerous known stability issues for such materials.² The same NCs at solid state but after the spray-drying process exhibited a

Figure 4. HAADF STEM images of (a) CsPbBr₃-LL NCs and (b) CsPbBr₃-SL NCs both 170 °C spray-dried with PMMA/P(BM)MA 50/50 w/w.

Figure 5. (a) Emission spectra and (b) PLQY of CsPbBr₃-LL and CsPbBr₃-SL NCs: in solution (green), in films obtained by drop casting of bare NCs (red) and after spray-drying process at 170 °C (blue). (c) XRD patterns of spray-dried CsPbBr₃-LL NCs (brown) and CsPbBr₃-SL NCs (purple) with XRD pattern of orthorhombic CsPbBr₃ ICSD 98-009-7851 (black).

different behavior. Compare to PL properties in solution, spray-dried CsPbBr₃-LL NCs PL maximum was red-shifted by only 2 nm and no shift was observed for spray-dried CsPbBr₃-SL NCs. Moreover, the FWHM was unchanged after spray-drying for both CsPbBr₃-LL and CsPbBr₃-SL NCs, indicating a good preservation of color purity and a better spatial separation of NCs compared to films with bare NCs. Thus, because the PL properties are linked to the NCs integrity, we assumed that the spray-drying encapsulation prevented more efficiently the NCs aggregation in solid-state, particularly in the case of encapsulated CsPbBr₃-SL NCs.

Concerning PLQY analyses (Figure 5b), when comparing NCs in solution and films of bare NCs, PLQY dropped from 72 ± 2 % to 42 ± 1 % for CsPbBr₃-LL NCs, and PLQY dropped even more drastically from 62 ± 2 % to 8 ± 1 % for CsPbBr₃-SL NC. The loss of PLQY for LHPs NCs in solid-state is not totally understood but it was demonstrated on bulk LHPs that

grain boundaries induced more non-radiative exciton recombination, limiting bulk LHP PLQY.⁶¹ Thus, the important loss of PLQY for bare CsPbBr₃-SL NCs film may be directly linked to the high quantity of grain boundaries induced by the use of short ligands which did not prevent NCs aggregation during solvent evaporation.⁷ This hypothesis is greatly supported by the STEM analyses (Figure 1b). Now, when comparing NCs in solution and after spray-drying, PLQY dropped from 72 ± 2 % to 47 ± 1 % for CsPbBr₃-LL NCs, and PLQY dropped from 62 ± 2 % to 35 ± 1 % for CsPbBr₃-SL NCs. The difference of PLQY conservation between NCs films and spray-dried nanocomposites was weak for CsPbBr₃-LL NCs, but for CsPbBr₃-SL NCs, the conservation of the initial solution PLQY (62 ± 2 %) is significantly improved after spray-drying encapsulation (35 ± 1 %) compare to NCs film (8 ± 1 %). These observations indicated a reduced number of aggregated NCs for the encapsulated CsPbBr₃-SL NCs, in good agreement with PL

Figure 6. Photostability over time of bare NCs and spray-dried NCs under continuous illumination (0.1 W/cm^2 ; blue LED 455 nm) in an on-chip configuration. (a) Images of the setup (inset: NCs on-chip). Normalized integrated PL evolution over time of (b) CsPbBr₃-LL NCs and (c) CsPbBr₃-SL NCs with bare NCs (black points) and spray-dried NCs (greens points). (d) Evolution of the corresponding emission spectrum of the LED down-converter with spray-dried CsPbBr₃-SL NCs.

analyses and STEM images. In general, the loss of PLQY during the spray-drying process may also have been caused by NCs surface ligands lost, which are known to have a very labile nature. Furthermore, the better PLQY conservation for spray-dried CsPbBr₃-SL NCs compare to bare NCs films strongly supported the benefit of the encapsulation.

Both spray-dried CsPbBr₃-LL and CsPbBr₃-SL NCs XRD patterns exhibited the expected orthorhombic crystalline structure of CsPbBr₃ perovskite.^{62,63} No additional phase formation due to thermal degradation is observed, which is usually a limiting aspect for LHPs.¹⁹ In other words, the encapsulation by spray-drying did not modify the structural properties of CsPbBr₃ NCs.

The spray-drying encapsulation in these specific conditions, not only preserved the initial morphological and structural properties of CsPbBr₃-SL NCs, but also improved the stability of their optical properties (PL, PLQY) compared to bare NCs in solid-state, which is a crucial problem for many applications. Despite these encouraging results, the final PLQY of 35 % of the CsPbBr₃-SL NCs / polymers nano-composite beads is relatively low compare to previous reported works on green emitting LHPs NCs / polymer composite films with good stability.^{28,30} To enhance the NC emission properties, many surface treatments have been explored in the literature reaching higher PLQY and stability,^{20,21} most of these studies have been conducted on CsPbBr₃-LL NCs. We believe that a similar post-synthesis surface passivation on CsPbBr₃-SL with appropriate short surface stabilizer (for example zinc bromide or tetrabutylammonium bromide) to keep the NCs inside the beads, would enhance the PLQY of bare NCs. In that way, the nanocomposites beads PLQY should directly benefit from the improvement of the NCs properties, with a better final PLQY. This aspect is under current investigation in our laboratories.

To evaluate the benefit of the spray-drying encapsulation on the CsPbBr₃ NCs photo-stability, we followed the evolution of

their PL emission under a continuous blue excitation in a LED down-converter device. Figure 6a shows the setup used for photo-stability measurements in ambient conditions. The NCs were excited by a blue LED ($\lambda = 455 \text{ nm}$) with a surface power density of 0.1 W/cm^2 , similar to industrial test conditions for backlighting materials in LCD displays. The bare NCs or spray-dried NCs were deposited on the blue-LED with an on-chip configuration, *i.e.* by drop-casting the NCs solutions directly on the chip (inset in Figure 6a). The emission stability of CsPbBr₃ NCs was evaluated by tracing the evolution of the integrated green PL signal.

For bare CsPbBr₃-LL NCs (black dots on Figure 6b), the green emission decreased rapidly and continuously when exposed to the blue excitation, indeed the normalized integrated PL dropped to 0.1 after only 13 h and to almost 0 after 50 hours. Such decrease in PL is generally attributed to a poor resistance against photobleaching and is in line with similar reported observations.^{5,18} The same degradation behavior was recorded for spray-dried CsPbBr₃-LL NCs (green dots on Figure 6b), even if a small normalized PL of 0.1 is retained after 30 h. The composite beads behaved like bare NCs because CsPbBr₃-LL NCs were not encapsulated in polymeric beads.

In the same way, green emission of bare CsPbBr₃-SL NCs decreased rapidly and continuously (black dots on Figure 6c), the normalized integrated PL intensity dropped to 0.1 after 55 hours. However, the green emission signal of the spray-dried CsPbBr₃-SL NCs was far more intense over time than the bare NCs (green dots on Figure 6c). Specifically, the normalized PL decreased down to 0.25 in the first few hours, but then slowly recovered and stabilized to an average value of 0.52 ± 0.04 from 50 to 200 hours. This better resistance to photobleaching demonstrated that the polymeric beads acted as a barrier against external environments. Likely the hydrophobic matrix limited the diffusion of ambient oxygen and moisture into the bead and slow down the photobleaching of CsPbBr₃ NCs. These results highlighted the benefits of the spray-drying encapsulation

process on CsPbBr₃ NCs, indeed when the CsPbBr₃-SL NCs were truly encapsulated we measured a photo-stability improvement.

As mentioned, the green emission of the spray-dried CsPbBr₃-SL NCs exhibited a specific behavior during the first hours of the experiment, the PL first decreased, then slowly increased, and finally stabilized for several hours (Figure 6d or in logarithmic scale Figure S6). Because the blue excitation power density was constant (minor variations compare to green variations), these PL variations were directly linked to NCs PLQY variations and thus indicated changes in the ratio between radiative and non-radiative recombination, especially for the first PL quenching and the following PL brightening. We note that for bare CsPbBr₃ NCs, only photobleaching due to photo-degradation was observed, thus PL quenching and brightening were probably induced by the spray-drying encapsulation. Previous studies on LHP materials have observed similar PL behavior.^{64,65,66} Galisteo-Lopez *et al.*,⁶⁴ observed strong PL photoactivation under continuous similar blue light excitation on hybrid organic-inorganic LHP bulk film. However, they did not observe early PL quenching, only a final photobleaching mostly due to moisture degradation. In the same way, Lorenzon *et al.*⁶⁶ studied the PL behavior of bare CsPbBr₃ NCs under different environmental conditions, they pointed out that PL quenching occurred with the presence of nonradiative defects, especially surface states and dangling bonds, leading to photogenerated carrier trapping. Based on these previous studies on LHP materials and others on Cd-based quantum dots,^{67,68,69} we assumed that in our case, the first PL quenching event was due to an increasing amount of non-radiative recombination due to carrier trapping. This might have been amplified by the creation of surface defects caused by ligands loss or ligands displacement during the spray-drying process. The following slow brightening indicates an increasing amount of radiative recombination compare to non-radiative, possibly due to trap state passivation. However, to fully understand this competition between PL quenching and brightening, further experiments of photostability under various atmospheres and deeper PL analyses (such as fluorescence lifetime) should be performed to get a better understanding regarding the impact of the polymer matrix on the PL behavior of the encapsulated NCs.

On-chip configurations are known to provide harsh test conditions with high thermal and optical exposure.⁷⁰ In our case, the thermal stresses were limited because sample local temperature was kept at 20-30 °C during the photo-stability measurements. This was achieved thanks to the relatively low light-power excitation combined with the use of a metal heat-sink in our setup. However, the current performances of the composite beads might be even more interesting for less stressful applications such as on-edge or on-surface NCs/LED configurations for backlighting.⁷¹

CONCLUSION

We have developed a new method to encapsulate CsPbBr₃ NCs within nanometric polymeric beads with a spray-drying process. The combination of acrylate polymers with specific chemical groups (PMMA and PBMA) matching the short ligands at the surface of the CsPbBr₃-SL NCs has allowed us to obtain NCs encapsulated within the beads. Through the spray-drying process, we managed to retain the optical and structural properties of the starting CsPbBr₃-SL NCs. The nano-

composite CsPbBr₃-SL NCs / polymer beads exhibited a PLQY of 35 % and an improved photo-stability at solid-state regarding to the bare CsPbBr₃-SL NCs. Indeed, we measured a stable NCs emission under in-use conditions with a LED down-converter, making these spray-dried NCs promising candidates for light-converting materials. We believe that the optical properties and the photo-stability of CsPbBr₃ NCs encapsulated by spray-drying process could be rapidly improved in the future by determining the right NCs surface passivation in the plethora of existing literature. Furthermore, efforts need to be done to reduce the polydispersity of the polymeric beads, and the use of different atomization or size-sorting techniques should help to achieve this objective. The synthesized nano-composite beads in this study could be used directly as final materials, or further incorporated in other types of matrix, or even functionalized. Thus, they may be used for many fields of application in the future, in particular for display applications, biological markers and security encoding.

In a more general context, there is room to explore the spray-drying nano-encapsulation of different types of nanocrystals (fluorescent, plasmonic, magnetic, etc.) in polymeric beads. The spray-drying process should offer a way to synthesize such nano-composite particles with a versatile, inexpensive, and scalable method, thus paving the way for industrialization.

METHODS

Materials. Lead bromide (PbBr₂, 98%), cesium carbonate (Cs₂CO₃, 99%), oleic acid (OA, 90%), poly(methyl methacrylate) (PMMA, M_w = 120 000 g.mol⁻¹), poly(butyl methacrylate-co-methyl methacrylate) (P(BM)MA, M_w = 150 000 g.mol⁻¹) and n-heptane (HEP, 99 %) were purchased from Sigma-Aldrich. Toluene (99.8 %), n-hexane (HEX, 95%) were purchased from Carlo Erba. 1-octadecene (ODE, 90 %) and oleylamine (OAm, 90 %) were purchased from Acros. Propionic acid (PrAc, 99.0%) was purchased from TCI. n-butylamine (BuAm, 98%) was purchased from Alfa Aesar. Propanol-2 (IPrOH, 98%) was purchased from VWR.

Synthesis of CsPbBr₃-LL NCs. The synthesis of CsPbBr₃-LL NCs was adapted from Protesescu *et al.*¹ 1.2 g of Cs₂CO₃ (3.7 mmol), 3.6 mL of OA (18.8 mmol) and 45 mL of ODE were introduced in a 100 mL three-neck round bottom flask and heated at 110°C under vacuum for 1 hour. The mixture was then heated to 130°C under nitrogen until the cesium oleate (Cs-OA) formation was completed. The Cs-OA solution was kept at 120°C to avoid solidification. In another 100 mL three-neck round bottom flask, 0.330 g of PbBr₂ (0.9 mmol) and 30 mL of ODE were dried under vacuum for 1 hour at 120°C. Then, 3 mL of OA and 3 mL of OAm were added at 120°C under vacuum, the solution was heated for 30 additional minutes. After complete solubilization of PbBr₂, the mixture was heated at 180°C under nitrogen with a vigorous stirring. Once the desired temperature was reached, 4.8 mL of Cs-OA (0.8 mmol) solution at 120°C was quickly injected. After 15 s the reaction was rapidly quenched by removing the heating mantle and cooling the flask with an ice water bath. For the purification step, the crude solution was centrifuged at a speed of 9000 rpm for 10 min. The supernatant was then discarded, and the precipitate was dispersed in 6 mL of toluene. The solution was centrifuged once more at a speed of 2000 rpm for 4 min and the supernatant was kept while the precipitate was discarded to remove the non-

stable nanocrystals. The obtained CsPbBr₃-LL NCs solution was stored under ambient conditions.

Synthesis of CsPbBr₃-SL NCs. The protocol synthesis of CsPbBr₃-SL NCs was adapted from Akkerman *et al.*⁷ A precursor solution of cesium propionate (Cs-PrA) at 2 M was prepared by dissolving 326 mg of Cs₂CO₃ in 1 mL of propionic acid at room temperature. Another precursor solution of PbBr₂ at 0.25 M was prepared by dissolving 184 mg of PbBr₂ in 2 mL mixture of PrAc:IPrOH:BuAm with a 1:1:1 volume ratio. Afterward, 6 mL of hexane, 3 mL of IPrOH and 27 μ L of Cs-PrA were added in a 25 mL round bottom flask. The mixture was stirred vigorously under ambient conditions (temperature and atmosphere) and 600 μ L of PbBr₂ solution was quickly injected. The solution immediately turned to green due to the formation CsPbBr₃-SL NCs. The crude solution was centrifuged at 1000 rpm for 2 min, then the supernatant was discarded and the NCs were dispersed in 6 mL of toluene. The obtained CsPbBr₃-SL NCs solution was stored under ambient conditions.

Spray-Drying Encapsulation. Typically, 900 μ L of CsPbBr₃-LL or CsPbBr₃-SL NCs of as prepared solutions were mixed with 6 mL of an acrylate polymer solution (4 wt% of PMMA:P(BM)MA 50:50 dissolved in toluene) in a specific vial. We estimated the NCs weight concentration to be around 0.2 wt%. The solution was stirred for 1 hour to ensure a good NCs dispersion in the polymer solution. The temperature of the tubular furnace was set at a temperature between 170 and 290 °C and the nitrogen pressure of the atomizer was set at 1.5 bar. Note that the perceived temperature inside the glass tube is around 50 °C lower than the tubular furnace temperature. The NCs / polymer solution was then plugged to the atomizer, the vacuum pump was turned ON and the nitrogen valve of the atomizer was immediately opened to initiate the atomization of the initial solution into a mist of droplets. Consequently, the mist was allowed to pass through the tubular furnace for solvent evaporation. During the process, the NCs / polymer solution continued to be atomized while the spray dried NCs were collected onto the hydrophilic polytetrafluoroethylene filter (0.22 μ m) placed beforehand at the outlet of the furnace. Once the solution was totally atomized (~ 5 min), the nitrogen valve, tubular furnace and vacuum pump were turned off. The dried powder of NCs / polymers composite collected on the filter was transferred and stored in a closed vial under ambient condition.

Preparation of LED Down-Converters. The “on-chip” configuration was used to evaluate the performance of CsPbBr₃ NCs in a light-emitting diode (LED) down-converter, with an OSRAM “Deep-blue LED W5SM Golden Dragon” as the blue excitation source. The powder of spray dried NCs was dispersed and sonicated in heptane. 2 μ L of the suspension was then deposited directly on the blue LED chip by drop-casting to form a uniform film of spray-dried CsPbBr₃ NCs after solvent evaporation. For bare CsPbBr₃ NCs, 2 μ L of the solution was directly deposited on-chip.

Photoluminescence Quantum Yield Measurement. The PL QY of the spray-dried NCs were measured with an integrating sphere spectrometer (Quantarus-QYPlus from Hamamatsu) and with thin sample to minimize diffusion and reabsorption effects. In order to be as close as possible to real application conditions, we used the same amount of powder as for the preparation of LED down-converters.

Photo-Stability. Photo-stability measurement were carried out under ambient conditions. The commercial blue LED had

an excitation wavelength of 455 nm and was used to optically pump the CsPbBr₃ NCs on-chip. The LED was powered with a DC current supply (LakeShore 101) at 1 mA to generate a surface power density of 0.1 W/cm². Indeed, for this working current we measured a light-power of 1.1 mW, divided by the 1 mm² LED-chip surface we obtained a light power density of about 0.1 W/cm². The LED was mounted with thermal paste on a printed circuit board attached to a cooler. The emitted signal from the on-chip NCs was collected by an optical fiber and detected with a spectrometer (UV-VIS OCEAN OPTICS STS) to obtain the emission spectrum of the LED down-converter. The emission stability of CsPbBr₃ NCs was evaluated by integrating the green PL signal over time.

Instrumentation. TEM/STEM observations were made on a Titan Themis 200 microscope (FEI/ Thermo Fischer Scientific) equipped with a geometric aberration corrector on the probe. The observations were made at 200 kV with a probe current of about 50 pA and a half-angle of convergence of 17 mrad. HAADF-STEM images were acquired with a camera length of 110 mm (inner/outer collection angles were respectively 69 and 200 mrad). Scanning electron microscopy (SEM) images were obtained with a JEOL JSM-7800F Prime for morphological characterization of the polymeric beads. X-ray powder diffraction (XRD) patterns were recorded with an Empyrean diffractometer from Malvern-Panalytical equipped with a monochromatized Cu K α radiation (λ = 1.540598 Å) and a PIXcel detector. The photoluminescence quantum yield (PLQY) of NCs was determined (with 5% of error bar) by using the Quantaurus-QYPlus UV–near-infrared absolute photoluminescence quantum yield spectrometer from Hamamatsu, with $\lambda_{\text{excitation}}$ = 460 nm. UV–visible absorption spectra were recorded on an Agilent Technologies Cary 60 UV–visible single-beam spectrometer. For NC solution, photoluminescence (PL) spectra were measured on a JASCO spectrofluorometer FP 8500, with $\lambda_{\text{excitation}}$ = 350 nm. For film and powder, PL spectra were recorded with the Hamamatsu PLQY spectrometer.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge via the Internet at <http://pubs.acs.org>

High resolution STEM, NC suspension pictures, SEM morphology analyses, photostability data.

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Author Contributions

FB designed and conducted experiments, analyzed data, and wrote the paper. MP analyzed data and finalized the paper. MD and AK designed the spray-drying process. GP conducted microscopic observations. GP and BD supervised the project and acquired funding. All authors have given approval to the final version of the manuscript.

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

FWHM, full width at half maximum; LED, light-emitting diode; LHP, lead halide perovskite; LL, long ligand; NC, nanocrystal; PL, photoluminescence; PLQY, photoluminescence quantum yield; PMMA, poly(methyl methacrylate); P(BM)MA, poly(butyl methacrylate-co-methyl methacrylate); SEM, scanning electron microscope; SL, short ligands; STEM, scanning transmission electron microscope; XRD, X-ray diffraction

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