ABSTRACT: The conventional strategy of synthetic colloidal chemistry for bright and stable quantum dots has been the production of epitaxially matched core/shell heterostructures to mitigate the presence of deep trap states. This mindset has been shown to be incompatible with lead halide perovskite nanocrystals (LHP NCs) due to their dynamic surface and low melting point. Nevertheless, enhancements to their chemical stability are still in great demand for the deployment of LHP NCs in light-emitting devices. Rather than contend with their attributes, we propose a method in which we can utilize their dynamic, ionic lattice and uniquely defect-tolerant band structure to prepare non-epitaxial salt-shelled heterostructures that are able to stabilize these materials against their environment, while maintaining their excellent optical properties and increasing scattering to improve out-coupling efficiency. To do so, anchored LHP NCs are first synthesized through the heterogeneous nucleation of LHPs onto the surface of microcrystalline carriers, such as alkali halides. This first step stabilizes the LHP NCs against further merging, and this allows them to be coated with an additional inorganic shell through the surface-mediated reaction of amphiphilic Na and Br precursors in apolar media. These inorganically shelled NC@carrier composites offer significantly improved chemical stability toward polar organic solvents, such as γ-butyrolactone, acetonitrile, N-methylpyrrolidone, and trimethylamine, demonstrate high thermal stability with photoluminescence intensity reversibly dropping by no more than 40% at temperatures up to 120 °C, and improve compatibility with various UV-curable resins. This mindset for LHP NCs creates opportunities for their successful integration into next-generation light-emitting devices.

KEYWORDS: lead halide perovskite, luminescence, nanocrystals, stability, core/shell
separable part of lead-containing devices. This RoHS regulation is independent of the encapsulation strategy and any potential leakage. At the same time, green-emitting LHP NCs offer superior optical properties compared to the commercially benchmarked InP-based QDs with PL QYs of about 85–90% (against 60% for InP) and narrow emission line widths of 20 nm (compared to 40 nm for InP). Furthermore, some estimates indicate that the superior absorption of blue light by LHP NCs over InP QDs may be sufficient to replace color filters (which can absorb up to 2/3 of emitted light in LCDs) with pixelated arrays of NCs. This can be a step forward toward more energy-efficient QD LCDs.

In this perspective, strong efforts have been dedicated toward improving the stability of colloidal LHP NCs. Still, colloidal LHP NCs struggle from several stability issues that hamper their deployment in applications such as LCD displays. First of all, ionic LHPs are moderately to highly soluble in polar solvents, which limits the processing after colloidal synthesis. Second, the highly dynamic binding of native ligands allows access of any damaging species to the surface of NCs. Third, the relatively low melting point of native ligands allows access of any damaging species to the surface of NCs. This hampers the post-synthetic processing of LHP NCs, especially in the presence of polar molecules and at elevated temperatures. Most of these issues can be overcome by properly isolating individual NCs from each other and from their environment. There are several common ways to accomplish this: embedding colloidal LHP NCs in a polymer film, glasses, lipid micelles, or in Pb-containing salts, coprecipitation of colloidal LHP NCs with salts, modifying their surface or capping the NCs with a shell. These approaches are well-established for conventional and structurally more rigid semiconductor NCs, typically made of II–VI, III–V, and IV–VI compounds. However, most of these known protocols require the treatment of NCs with polar solvents or molecules which, in the case of LHPs, accelerate the ripening of NCs. Recently, we and several other groups have proposed a synthetic approach which overcomes this problem by isolating NCs from each other already during the nucleation step. Specifically, LHP NCs were synthesized inside a chemically robust mesoporous matrix that prevented NCs from ripening and retarded the dissolution of LHPs in the presence of polar moieties.

These previous works have revealed several specific attributes of LHP NCs that suggest re-evaluating their engineering. First, as a result of their defect-tolerance, LHP NCs do not require passivation for bright PL as they are rather insensitive to dangling bonds. In addition to this, their highly dynamic lattice allows their surface to rearrange to adhere to a variety of materials: SiO2, Al2O3, TiO2, CsPbBr3, etc. Finally, LHP NCs are the only currently known semiconductor material to exhibit bright emission with PL QY approaching unity in the weak-confinement regime. This allows them to be synthesized with high polydispersity and large sizes, while still retaining exceptionally narrow emission line widths down to 18 nm.

Additionally, these findings suggest that there is no need to stick to the concept of thin, epitaxial shelling of individual QDs when using LHP NCs. In contrast to conventional QDs, where the complete and uniform epitaxial shelling of well-isolated colloidal particles is required, LHP NCs can retain their excellent optical properties even when directly embedded into non-epitaxial micrometer-scale composites or templates. The use of such micron-sized composites allows us to address a critical issue in QD-based backlit films for LCDs — poor light out-coupling efficiency. This issue is related to the wave-guiding of light within the emissive layer, which has two primary loss mechanisms. First, it reduces the fraction of light emitted from the frontal plane of the device toward the liquid crystal layer. Second, the wave-guiding increases the effective optical path and thereby increases the likelihood of reabsorption by other QDs. These losses can be particularly high in QD-based down-converting layers as a result of their generally small Stokes shifts, leading to increased overlaps between absorption and emission bands. A common strategy toward reducing these losses involves the incorporation of highly scattering microparticles (e.g., SiO2, ZnO, BaSO4, ZrO2) into the down-converting layer to improve the light out-coupling efficiency. Herein we propose a facile, non-colloidal synthetic route that accomplishes both aforementioned goals — creating bright LHP emitters along with photonic engineering for light-outcoupling. Specifically, luminescent APbX3 NCs (A = Cs or FA; X = Cl, Br, I) were heterogeneously nucleated onto the surface of inorganic microcrystalline carriers (nanocrystals on carriers; NCCs). We show that the anchoring of LHP NCs significantly stabilizes them against merging and allows them to

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Scheme 1. Encapsulation of LHP NCs into Inorganic Microcrystals

“In the first step (Ia–c), LHP NCs heterogeneously nucleate and grow on the surface of the microcrystalline carriers (NaX, KX, RbX, CsPbX3, (Cs,Rb)2PbX4, PbX2, MgX2, CaX2, SrX2, BaX2, and ZnX2 where X = Cl, Br, I or their mixtures.) In Ic, the crossed-arrows indicate that inter-NC coupling is strongly diminished. The obtained NCCs are then shelled with NaBr in the second step of the synthesis through the direct reaction of amphiphilic Na and Br precursors in an apolar solvent (IIa,b). The entire process yields the final, shelled polycrystalline NCC/NaBr particles.
be shelled with transparent and chemically robust NaBr salt matrices. The final shelled NCC/NaBr exhibit improved stability against a vast variety of solvents and can be used in processes that are otherwise inaccessible or very harmful for colloidal LHP NCs, such as encapsulation into industrially important acrylate-based polymers including silicone urethane acrylate, hydroxyethyl methacrylate, and poly(vinyl acetate).89,90 Furthermore, the presence of highly scattering, polydisperse microcrystals with sizes in the range of 0.1–1 μm hinders wave-guiding and improves the efficiency of light out-coupling, making these composite materials well-suited for use in LCD displays.88,89

RESULTS AND DISCUSSION

The synthesis begins with the concomitant crystallization of an inorganic salt, hereafter called a carrier, and LHP NCs from a single solution in a polar solvent. Crystallization can be induced either by evaporating the solvent or by the addition of a suitable antisolvent. The concentrations and solvents are chosen in such a way that the carrier microcrystals start to precipitate first and enable the heterogeneous nucleation of LHP NCs, which is followed by their growth (Scheme 1). Through this process, the LHP NCs are anchored to the surface of the carrier (NCC) and are thereby stabilized against merging. This also allows for further processing in the presence of polar molecules. In the next step, a shell of an alkali halide or another inorganic salt can be grown onto these composite materials, thus completing the encapsulation of the LHP NCs (Scheme 1). The proposed approach has been tested for the encapsulation of Cs- and FA-based LHP NCs into NaX, KX, RbX, Cs,PbX₆, MgX₂, CaX₂, SrX₂, BaX₂, and ZnX₂ matrices where X = Cl, Br, I or their mixtures. We selected these carriers due to their transparency to visible light and their suitable solubility in polar aprotic organic solvents, which is typically a few times lower than the solubility of LHPs. Some of these carriers (MgBr₂, CaBr₂, ZnBr₂) were too hygroscopic and therefore led to LHP NCs with poor stability. From all the other carriers, each carrier-LHP pair required the molar ratio to be adjusted due to the difference in carriers’ solubilities, as discussed below.

To prepare these materials, solutions of an alkali-halide (NaBr, KBr, or RbBr), CsBr or FABr, and PbBr₂ in dimethyl sulfoxide with a small addition of N-methylformamide are correspondingly mixed in a desired molar ratio (see SI and Table S1 for details). This mixture was then drop-cast onto a glass substrate and typically dried at 70 °C with 25–50% relative humidity (RH) for 3 h and then allowed to cool to room temperature. The synthesis produces a homogeneous, microcrystalline powder with morphologies and optical properties that are very different from either of the precursors (Figures 1a and S1).

Confocal and optical microscopy shows roughly faceted microcrystals that often exhibit a tetrahedral habit, which is typical for alkali halides (Figure 1b,c). These microcrystals are only slightly colored but yield bright green luminescence under UV-excitation. This combination of crystal faceting and bright emission implies that the emission centers are mainly localized on the surface of the microcrystals and that they are not, or at least not always, embedded inside. Confocal microscopy confirms that LHP NCs are primarily localized on the surface of microcrystals (Figure S2). The high polydispersity is favorable for these microcrystals, as it can significantly improve the total scattering within the system, resulting in improved out-coupling efficiencies if introduced as down-converting layers in LCDs.

Scanning transmission electron microscopy in secondary electron (SE) and high-angle annular dark-field (HAADF-STEM) modes confirm the presence of heavy-atom nanocrystalline inclusions on or near the surface of the microcrystals (Figures 1d–f and S3). We note that electron microscopy of the interior of microcrystals is not feasible due to their large thickness. Furthermore, electron microscopy of such composite materials is generally difficult due to the high volatility of metal halides under an electron beam.92 However, STEM qualitatively shows the high concentration of LHP NCs and their small size (ca. 5–10 nm), which is in agreement with a PL peak position of 510 nm for this sample (RbBr:CsPbBr₃, 10:1) and corresponds to that of colloidal 8 nm NCs.1,43 Energy-dispersive X-ray spectroscopy shows the presence of Cs, Rb, Pb, and Br, which together with the HAADF-STEM images imply that the carrier consists of alkali bromide, whereas bright NCs are Pb-based (Figure S3). Furthermore, powder X-ray diffraction (XRD) confirms the presence of a crystalline carrier (alkali halides or Cs,PbBr₃) as the dominant phase (Figure S4). However, XRD measured on a conventional powder diffractometer is not able to reveal the presence of Cs,PbBr₃ NCs due to the significant, size-related broadening of relevant reflections and the small amount of LHP compared to
the carrier. XRD measured at a synchrotron light source (SLS XRD) reveals the broad modulation of the background that coincides with CsPbBr$_3$ (Figure S5, see SI for details). This modulation indicates that CsPbBr$_3$ is present in the form of NCs with sizes roughly estimated to be below 10 nm, similar to the NCs seen in the STEM images.

The variation of the carrier:LHP ratio is the main tool for controlling this synthetic process. An increasing ratio changes the area available for the heterogeneous nucleation of LHP NCs and therefore the number of nuclei. This allowed us to tune the average size of LHP NCs, which can be roughly determined from the PL spectra for medium to small LHP NCs by using a sizing curve reported earlier for colloidal 43 and free NC emitters.93,94 We note that such narrow emission is one of the key factors required for color pure Rec.2020 standards for next-generation displays.95

As mentioned above, the dilution of CsPbBr$_3$ NCs down to a carrier:LHP molar ratio of 50:1 does not change the wavelength of the PL maximum. However, this dilution significantly improves the PL QY of unshelled NCCs (Figure 2b). In the case of a high LHP loading (KBr:CsPbBr$_3$ ratio below 10:1), the formation of CsPbBr$_3$ NCs on KBr carriers competes with the growth of bulk CsPbBr$_3$ in the form of large CsPbBr$_3$ microcrystals. At a KBr:CsPbBr$_3$ molar ratio of 30:1, the formation of CsPbBr$_3$ microcrystals is limited, and an additional impurity of orange, non-luminescent microcrystals of CsPbBr$_3$ can also be observed (Figure S7). At slightly lower LHP loading (KBr:CsPbBr$_3$ molar ratio from 20:1 to 50:1), this impurity disappears, yet the PL peak position remains nearly unchanged in the range of 515−520 nm (corresponds to ∼14−20 nm large NCs). Even lower LHP loading (KBr:CsPbBr$_3$ ratio above 50:1) leads to an insufficient amount of precursors. In this case, the diffusion-limited growth of CsPbBr$_3$ NCs results in a decrease of the average size and a blueshift of the PL maximum to 495 nm, which corresponds roughly to 7 nm large NCs (Figures 2a and S6).

For various carriers, the PL starts to blueshift at slightly different LHP:carrier ratios (Figure S6). At very low LHP loading (KBr:CsPbBr$_3$ ratios from 100:1 to 1000:1), the PL further shifts to 480 nm (∼5 nm NCs), and a fraction of pure KBr microcrystals with perfect tetrahedral habits and without PL can be observed (Figure S8).

Despite the lack of ligands or other additives that traditionally control the nucleation and growth of NCs, these NCs still exhibit relatively narrow PL in the weak confinement regime (PL peak position at >515 nm corresponding to NCs with sizes above 14 nm). A typical PL full-width-at-half-maximum (fwhm) for green-emitting powders is about 20−22 nm for CsPbBr$_3$ and 25−27 nm for FAPbBr$_3$. This is comparable to the fwhm of colloidal8,12 and templated8 LHP NCs and much narrower than that of state-of-the-art green Cd-free NC emitters.93,94 We note that such narrow emission is one of the key factors required for color pure Rec.2020 standards for next-generation displays.95

Figure 2. Optical properties of unshelled CsPbX$_3$ NCCs. (a) PL tunability of CsPbBr$_3$@KBr NCCs by variation of KBr:CsPbBr$_3$ molar ratio; the average size of LHP NCs progressively decreases with increasing carrier:LHP ratio. (b) PL QY dependence on carrier:LHP ratio for the CsPbBr$_3$@KBr system. The highlighted areas correspond to different regimes: orange, coexistence of LHP NCs and bulkier LHP microcrystals that reabsorb emitted light; green, the optimal range, where LHPs are mainly present in the form of large NCs (weak confinement regime or without quantum confinement); and blue, LHP NCs are small and exhibit medium or strong quantum confinement. (c) Time-resolved PL spectra of CsPbBr$_3$@KBr NCCs with various KBr:CsPbBr$_3$ ratios; the pumping intensity 10 nJ/cm$^2$. (d) A photograph depicting various NCCs dispersed in a variety of containers such as plastic balls, glass dishes, and capillaries to demonstrate the visual tunability of their emission color through the size and composition of LHP NCs.

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Within the range where the PL QY varies slightly (40:1 to
100:1 carrier:LHP ratio), the PL shifts from 520 to 495 nm
and the PL decay becomes 3.5× faster. This trend is in
agreement with the PL lifetime dependence on NC size that
has been reported earlier for colloidal CsPbBr3 NCs: smaller
NCs have faster radiative relaxation rates at room temperature
than larger ones. At the same time, we found the PL decay
to be nearly independent of the carrier if NCs of a similar
size are compared (Figure S9).

Although all of the studied alkali-halides behave similarly as
carriers, CsX cannot be easily compared to the others due to
the presence of intermediate compounds in the CsX-PbX2
system. Instead, these intermediate compounds can themselves be
used as carriers. This extends the concept of concomitant
iso-anionic crystallization of LHP NCs and carriers to a fully
iso-atomic system, where CsPbX3 NCs are grown on CsX-PbX2-
based carriers. The pseudobinary CsBr-PbBr2 system contains
three compounds: CsPbBr3, CsPb2Br5, and Cs4PbBr6.97 The
last two melt incongruently, indicating that the formation of
CsPbBr3 and binary parent compounds is more energetically
favorable (Figure S10). The formation of CsPbBr3 NCs on the
surface of CsPbBr3 can, however, be favored by the fact that
these two phases have very similar atomic positions and
symmetry along several planes.76

The optical properties of the resulting CsPbX3@Cs4PbX6 powders are similar to those synthesized on alkali halide carriers. By adjusting the anion composition in CsPbX3@Cs4PbX6 NCCs, the emission wavelength can be tuned between 400 nm (corresponding to CsPbCl3) and 700 nm (corresponding to CsPbI3), as shown in Figure S11. Only partial anion exchange was possible as compositions with ~15–50% of heavier anion show two PL bands indicating phase separation, analogous to previous reports for the bulk CsPbBr3-CsPbI3 system. For alkali-based
matrices, the range where solid solutions were unstable was
generally broader, and only ~20% of the heavier halide could be exchanged with a lighter one for both the Br/Cl and I/Br systems. Despite the appealing optical properties of CsPbX3@ Cs4PbX6 NCCs, we did not consider them for further
investigation because the CsPbX3 carrier significantly
increases the overall Pb content of the composite material.

Instead, only NCCs grown on Pb-free carriers have been
shelled with salt matrices.

While anchoring LHP NCs to the carrier surface minimizes
the probability of NC merging, it does not protect NCs from
their environment. In order to fully encapsulate NCCs into salt
matrices, we grew an additional alkali halide shell on the NCC
microcrystals. To do so, we developed a polar-solvent-free
shelling technique based on the reaction of amphiphilic Na+
and Br− salts, namely sodium docusate (AOT) and
didodecylammonium bromide (DDAB) in toluene. Both salts
are highly soluble and slowly react in toluene, leading to the
precipitation of NaBr over the course of 12 h. The introduction
of Na+, K+, or Rb-based NCCs into this system results in the heterogeneous nucleation and growth of NaBr around the NCC, resulting in the final NCC/NaBr (Scheme 1).

These shelled microcrystals can be obtained in the form of
fairly stable dispersions (Figure 3a) or powders if all surfactants are washed away (Figure 3b). The shelled NCC/ NaBr exhibit a random non-uniform spatial distribution of
emission centers inside the microcrystal (Figure 3c). This is
in stark contrast to the unshelled NCCs, where LHP NCs are
localized primarily on the surface (Figure 1b,e,f). This fact,
together with the clearly polycrystalline nature of the shelled

Figure 3. Shelled CsPbBr3@KBr/NaBr microcrystals: (a) suspension in toluene under UV light and (b) optical and (c) confocal
microscopy. (d) Comparison of PL spectrum of initial CsPbBr3@ KBr NCC (blue curve) and shelled NCC/NaBr (green curve). (e)
Time-resolved PL of CsPbBr3@KBr NCC and shelled CsPbBr3@ KBr/NaBr in comparison with colloidal CsPbBr3 NCs.

microcrystals, indicates that the NaBr grows heterogeneously
on the surface of NCCs but not separately.

The dissolution and merging of LHP NCs could have
potentially been the main issues encountered upon treating
NCs with polar DDAB and AOT species, and this was indeed the case when colloidal CsPbBr3 NCs were subjected to an
analogous shelling procedure. In contrast, the anchored NCCs
remain stable and similarly bright after shelling. The PL peak
position remains nearly unchanged (Figure 3d), and the PL
fwhm slightly narrows. This may be primarily due to the
growth of any small LHP NCs on the surface, which pushes them toward weaker quantum confinement (Figure 3d). The overall stability of the PL peak position and profile indicates that anchored NCCs do not dissolve during shelling
procedure. On average, the PL QY remains unchanged or it
even slightly increases (Figure 3d). Furthermore, the average
measured lifetime increases from about 25 ns for optimal
CsPbBr3 NCCs to 45 ns for shelled CsPbBr3 NCC/NaBr (Figure 3e).

In order to check if anchored LHP NCs can merge during
the shelling procedure, we investigated the PL temperature
dependence of the final, shelled NCC/NaBr samples (Figure 4).
At room temperature, the PL of bulk CsPbBr3 is very weak
and cannot be detected in the presence of bright NCs. However, the PL of bulk CsPbBr3 impurities, if present, can be
well resolved at 4–15 K when it becomes much brighter and
narrower with a peak position at 539 nm (Figures S12). We
have found that the PL of bulk impurities can be readily
differentiated from the PL of even very large NCs which emit
at 525 nm at room temperature and are expected to be above
30 nm in size (Figures S12 and S13).43 Our optimized
 CsPbBr3@KBr/NaBr powder exhibits PL at 520 nm at room
temperature and therefore should contain smaller LHP NCs.
This allowed us to resolve any potential impurity of bulk
CsPbBr3 if it would have been present in the sample. Figure 4a
indicates that the PL spectrum collected at 15 K does not show
a sharp line at a wavelength of 539 nm (2.300 eV). This
indicates that our anchored LHP NCs do not merge (at least
not to the point that they grow above 30 nm in size) during
the shelling process.
The overall PL dependence on temperature for the shelled CsPbBr$_3$@KBr/NaBr is very similar to that of colloidal LHP NCs. The PL redshifts to 2.331 eV (532 nm) upon cooling to 15 K and narrows down to $20^{\pm}40$ meV. This fwhm indicates that the size distribution of CsPbBr$_3$ NCs is roughly two times broader than the best colloidal counterparts. The fast component of the radiative decay rate accelerates from about 10 to 0.6 ns at 15 K. Those values are typical for large (15$^{\sim}20$ nm) colloidal LHP NCs.

In addition to preserving or even enhancing the optical properties of LHP NCs, the fully shelled LHP NCCs/NaBr also demonstrate good stability against many polar solvents. They withstand sonication in pure acetone, acetonitrile, ethanol, N-methylpyrrolidone, $\gamma$-butyrolactone, tetramethylurea, and triethylamine (Figure 5). In contrast, colloidal CsPbBr$_3$ NCs either completely dissolve or merge even in the presence of minor quantities of polar molecules (9 vol % in toluene) and consequently suffer a significant decrease in their PL QY. The shelled NCCs/NaBr instead dissolve only slightly in some solvents and retain their high PL QY. We attribute the enhanced stability to the fact that the aforementioned solvents, while able to dissolve or degrade LHPs, are rather poor solvents for alkali halides. As a result, only fully shelled LHP NCCs can survive treatments with such solvents, whereas poorly shelled or unshelled ones dissolve. This aspect can be used to wash out poorly shelled NCCs from the ones which are properly shelled.

Given that shelling protects LHP NCCs from attack by many polar molecules and stabilizes them against merging, one can now use these powders in many post-synthetic processes that would otherwise diminish the optical properties of colloidal LHP NCs. For example, one can perform polymerization with numerous monomers or embed these microcrystals into polymers without significant loss of PL QY (Figure 6a-c). As there are many polymers with very low water and oxygen permeability and many of them can be used as an encapsulant for such materials, we chose to investigate those which could further enhance the stability of these shelled LHP NCCs. Therefore, polystyrene, cyclic olefin copolymer TOPAS, and various UV-curable monomers have been tested including methyl methacrylate, lauryl methacrylate, silicon urethane acrylate (Miramer SIU2400), bisphenol A glycerolate diacrylate, NOA 63 with or without additives of ethylene glycol dimethacrylate, 2-hydroxyethyl methacrylate, vinyl acetate, and isobornyl acrylate. In all of these cases, the PL QY of NCC/NaBr did not drop after embedding them into a polymer encapsulant. This is again in stark contrast to colloidal CsPbBr$_3$ NCs which are known to often lose their PL QY after being embedded into polymers. At elevated temperatures, all samples show decreased PL QY, which is an intrinsic property of LHPs. The shelled FAPbBr$_3$ NCs exhibit the best thermal stability (Figure 6d,e). At 40$^{\sim}50$ °C, which is a typical operating temperature for backlight displays, their PL intensity only decreases by about 5%. At 120 °C, the PL intensity decreases by 40%. However, we found that briefly heating (~20 min at temperatures above 100 °C) does not permanently degrade the samples; the PL intensity fully recovers when samples are cooled down to room temperature (Figure 6d). Similarly, the PL peak position blue shifts by about 8 nm upon heating to 120 °C but returns to its original
CsPbBr₃ NCC/NaBr samples showed notably higher stability regime. After 190 h under such harsh conditions, the shelled allowed us to probe the material degradation in an accelerated conditions than required for real display applications. This inorganic matrix with a polymer encapsulant.

NCs, and it is enabled by the combination of a robust knowledge, this is the best stability reported so far for LHP

position after cooling (Figure 6e). Additional heating/cooling cycles can be repeated with complete reversibility. In contrast, colloidal NCs embedded into polymer films do not exhibit this thermal stability and instead quickly merge (Figures 6d,e). In order to verify the long-term stability of NCC/NaBr microcrystals, we embedded them into polymer films and performed three reliability tests: (i) at 80 °C, (ii) at 120 °C, and (iii) at high humidity and elevated temperature (95% RH, 50 °C). These tests were performed in notably harsher conditions than required for real display applications. This allowed us to probe the material degradation in an accelerated regime. After 190 h under such harsh conditions, the shelled CsPbBr₃ NCC/NaBr samples showed notably higher stability compared to colloidal NCs (Figure 6f): about 65% of the initial PL QY remained after 190 h at 80 °C, and the PL QY drop during the humidity test was negligible (although the overall brightness dropped a bit, probably due to partial diffusion of water inside the polymer.) To the best of our knowledge, this is the best stability reported so far for LHP NCs, and it is enabled by the combination of a robust inorganic matrix with a polymer encapsulant.

CONCLUSIONS

In summary, we propose a two-step approach to the synthesis of LHP NCs embedded into robust Pb-free microcrystalline, inorganic salt matrices. The key point of this approach is the initial concomitant crystallization of LHP NCs and salt carriers. By anchoring LHP NCs to the carrier, they are stabilized against merging and can be coated with an optically transparent inorganic shell. For this second step, we developed a method that involves the direct reaction of amphiphilic Na and Br precursors in polar-solvent-free media, resulting in the precipitation of NaBr on the surface of salt carriers and LHP NCs. This results in NaBr-shelled-NCCs with optical properties on par with the best colloidal LHP NCs, including high PL QY of ~90%, pure PL colors with line widths as narrow as 20 nm for green LHPs, and PL tunability through both NC size and anion composition. At the same time, the stability of these powders toward polar moieties, such as ethanol, acetonitrile, γ-butyrolactone, or acrylates, is significantly improved due to the complete isolation of LHP NCs from each other and from the environment. This permits the use of shelled LHP NCs in processes which otherwise degrade the optical properties of colloidal LHP NCs. Finally, the introduction of non-absorbing inorganic shells and matrices increases their overall scattering to facilitate improved out-coupling efficiencies for down-converting films in LCDs.

EXPERIMENTAL SECTION

Synthesis of LHP NCs on Alkali Halide Carriers. The relevant solutions from Table S1 were mixed in a desired ratio, homogenized by vortex mixing, drop-casted onto a glass substrate, and heated to 70 °C for 5 h (for Cl- and Br-based compositions) or to 200 °C for 10 min (for I-based compositions). For FAPX₃ NCCs (X = Br, I), an excess of FAX in respect to PbX₂ was used.

Shelling of NCs-on-Carrier (NCC) with NaBr. NCC powders were thoroughly ground or mildly ball-milled. The obtained fine powder (10 mg) was dispersed in 2 mL of a DDAB solution in toluene (0.5 M) and sonicated for 5 min. The resulting dispersion was stirred, while 0.5 mL of an AOT solution in toluene (2 M) was added dropwise over the course of an hour. The reaction mixture was kept stirring for the next 12 h. The final dispersion was washed with toluene and ethyl acetate, dried in vacuum, and stored inside a glovebox.

Encapsulation of NCC and NCC/NaBr into PS or TOPAS Polymers. The desired amount of NCC/NaBr powder was dispersed in a polymer solution in toluene (10 wt %) and cast onto a glass substrate and dried at 50 °C for 1 h.

Example of the Encapsulation of NCC/NaBr into UV-Cured Polymers. The desired amount of NCC/NaBr powder was added to a distilled LMA:EGDMA mixture (4:1) with 0.1% of Irgacure 819. The obtained mixture was cast onto a glass substrate and cured for 15 min under 20 mW/cm² flux (365 nm).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.9b05481.

Details of the materials synthesis, encapsulation into polymer matrices, characterization techniques and stability tests, additional supplementary figures, optical microphotographs, confocal and electron microscopy
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