Mechanosynthesis of polymer-stabilized lead bromide perovskites: Insight into the formation and phase conversion of nanoparticles

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ABSTRACT

The application of polymers to replace oleylamine (OLA) and oleic acid (OA) as ligands for perovskite nanocrystals is an effective strategy to improve their stability and durability especially for the solution-based processing. Herein, we report a mechanosynthesis of lead bromide perovskite nanoparticles (NPs) stabilized by partially hydrolyzed poly(methyl methacrylate) (h-PMMA) and high-molecular-weight highly-branched poly(ethyleneimine) (PEI-25K). The as-synthesized NP solutions exhibited green emission centered at 516 nm, possessing a narrow full-width at half-maximum of 17 nm and as high photoluminescence quantum yield (PL QY) as 90%, all-inorganic CsPbX₃ (X = Cl, Br, or I) perovskite nanoparticles (NPs) have attracted tremendous interest especially in photonic applications [1, 2], including electrically-driven light-emitting diodes (LEDs) [3, 4], color-conversion white LEDs (WLEDs) [5, 6], lasers [7, 8], and X-ray scintillators [9, 10]. Furthermore, the relatively low formation energy and high defect tolerance of these lead-halide perovskites enable the synthesis of their highly fluorescent nanocrystals via relatively simple synthetic procedures at low-temperature [11–13]. However, the labile surface, ionic nature, and metastable structure of perovskite materials cause them to suffer from poor stability and durability, especially in the solution-processing steps [14, 15]. For example, the process of precipitation and concentration of perovskite NPs using polar solvents is often accompanied by a large decrease in PL QY due to the loss of dynamic oleylamine (OLA) and oleic acid (OA) ligands [15]. Additionally, strong polar solvents, such as methanol and ethanol, will completely quench the fluorescence of OLA/OA-capped perovskite nanocrystals [14]. To improve the stability of perovskites, previous reports focused on the following three strategies: (i) modification of the OLA/OA-capped perovskite surface with stronger binding ligands [14–19]; (ii) encapsulation of perovskite materials into inorganic oxides [20–25] or hydrophobic polymers [5, 23, 26]; and (iii) construction of various composite heterostructures with different perovskite phases [6, 27–32]. The relatively weak interactions between perovskite nanocrystal and OLA/OA...
opened up many opportunities for further surface design and modification [15, 33]. Ligands, such as zwitterionic molecules [14], benzenesulfonic acid [15], didodecyl dimethylammonium bromide (DDAB) [16], phosphine ligands [17, 19], and 2,2′-iminodibenzoic acid (IDA) [18] with stronger binding to the nanocrystal surface were used to enhance the PL QY as well as the durability and resistance to polar solvents of the nanocrystals. Generally, most of the inorganic oxides, such as silsesquioxane [23, 25], SiO2 [21, 24], AIO [20, 24], and glass [22], can physically isolate the perovskite materials from the surrounding chemical environment, thus significantly improving their stability. However, this isolation is often accompanied by a significant reduction in solution processability for encapsulated materials. Some hydrophobic polymers, such as polyvinylidene fluoride (PVDF) [5], poly(methyl methacrylate) (PMMA) [23], and polystyrene (PS) [26], can not only play a role similar to inorganic oxides, but also impart excellent solution processability, which is very favorable for solution-processable applications.

As solely the CsPbBr3 phase exhibits high PL among many other known phases of cesium lead halide perovskites [34, 35], the stability of this phase may not only be improved by its embedding in a foreign robust material, but also by combining it with other non-fluorescent phases of the perovskite family, such as CsPbBr3 and CsPb2Br5. Indeed, the relatively stable light-emitting heterostructures of core-shell CsPbBr3/CsPb2Br5 [29], CsPbBr3 embedded in CsPbBr3 [6, 28], CsPbBr3 blended with CsPbBr3 [27, 31], and CsPbBr3 blended with CsPbBr3 [30, 32] were reported. In addition to the positive influence on the stability, these CsPbBr3 and CsPb2Br5 phases with wide energy bandgap can passivate surface defects of the CsPbBr3 phase, thus improving its PL QY. This kind of heterostructures are of special practical interest, as they may be created by relatively versatile and easily up-scalable methods (e.g., one-pot combination with h-PMMA) results not only in the improvement of the emitting and non-emitting perovskite-phases.

In our recent work, we reported that the CsPbBr3-CsPb2Br5 to CsPbBr3-Cs4PbBr6 transition could be used to significantly enhance the PL QY of the resulting NPs [36]. The amount of PEI had a significant effect on the morphology and optical properties of the resultant NPs, while the amount of h-PMMA did not. Therefore, in the present work, we fixed the amount of h-PMMA in grinding at 0.1 g and studied the effect of various amounts of PEI-25K (0, 0.01, 0.015, 0.02, 0.025, and 0.03 g) on the properties of the NPs.

2 Results and discussion

Perovskite NPs stabilized by h-PMMA/h-PEI were prepared based on our previous work with some modifications [36]. Specifically, mixtures of equivalent molar amounts of PbBr2 and CsBr were ground by a ball mill. The appearance of a yellow powder indicated the formation of bulk CsPbBr3. Next, the polymer of h-PMMA with a 10% degree of hydrolysis and PEI-25K dissolved in dichloromethane (DCM) were added and the mixture was subjected to further grinding. The resulting product was further diluted and collected with DCM. After centrifugation, the DCM-supernatant was replaced with pure toluene allowing to obtain toluene solutions of NPs. Our previous work showed that the amount of PEI had a significant effect on the morphology and optical properties of the resultant NPs, while the amount of h-PMMA did not. Therefore, in the present work, we fixed the amount of h-PMMA in grinding at 0.1 g and studied the effect of various amounts of PEI-25K (0, 0.01, 0.015, 0.02, 0.025, and 0.03 g) on the properties of the NPs.

2.1 Morphology and composition

The typical h-PMMA-capped NPs exhibit a cubic shape with a uniform size of 29.3 ± 6.1 nm (Fig. 1(a)), an elemental ratio of Cs:Pb:Br = 1.0:1.1:2.9 (Fig. 1(a)) and the orthorhombic phase of CsPbBr3 (Fig. 1(g)). The introduction of PEI causes the resulting NPs to change from cubes to larger spheres of a less regular size. Spots with a stronger contrast can be recognized in the transmission electron microscopy (TEM) images of the individual NPs (Figs. 1(b)–1(f)). As the amount of PEI added to the synthesis increases, X-ray diffraction (XRD) peaks corresponding to the CsPbBr3 phase gradually diminish, as shown in Fig. 1(g) and Fig. S2 in the Electronic Supplementary Material (ESM). Simultaneously, the relative intensity of the diffraction peaks of CsPbBr3 and CsBr gradually increases (Fig. 1(g)). These changes are accompanied by the appearance of an unspecified background, which could be associated with an amorphous phase (Fig. S2 in the ESM). The resulting NPs modified by 0.03 g of PEI show the dominating diffraction peaks of the crystal phases of CsPbBr3 and CsBr with almost completely disappeared signals related to CsPbBr3 (Fig. 1(g)). Meanwhile, the elemental ratio of Pb and Br relative to Cs in the resulting NPs increased first, reached its maximum (Cs:Pb:Br = 1.0:10.1:19.7) at the PEI amount of 0.025 g, and decreased again with the higher concentrations of PEI added (Fig. S3 and Table S1 in the ESM). As will be shown below, the NPs synthesized in the presence of 0.025 g of PEI-25K possess the highest PL QY of 85% among all considered samples. The majority of these NPs appear in TEM as uniform spherical particles containing many spots of a higher contrast material. Three crystal phases of CsPbBr3, CsPb2Br5, and CsBr, as well as amorphous phases are evidenced in this sample by powder XRD. The elemental ratio is found to be Cs:Pb:Br = 1.0:10.1:19.7.
2.2 Formation and phase conversion of the nanoparticles

Based on the above description of the morphology and phase composition, the following questions are especially worth of further discussion: i) Why do these NPs prepared by ball milling exhibit such uniform size? and ii) what exactly are the particles observed in the bright-field TEM images? In order to address these questions, a representative sample synthesized with 0.025 g PEI-25K was further characterized by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) imaging combined with element mapping based on energy dispersive X-ray spectroscopy (EDX) analysis to determine the composition of the individual particles. As shown in Figs. 2(a)–2(c) and Figs. S4(a)–S4(c) in the ESM, approximately 15% of the NPs (highlighted by blue circles) are characterized by a Cs-rich and Pb/Br/N-deficient elemental composition. The rest of the particles exhibit a Cs-deficient and Pb/Br/N-rich elemental composition. Furthermore, high-resolution TEM imaging was carried out to test the crystallinity of the NPs. While there are no indications for lattice fringes in the case of the Cs-deficient particles pointing to their amorphous nature, lattice arrangements are observed for the Cs-rich NPs, which are hence crystalline (Fig. 2(d)). The crystal lattice parameters match the lattice parameters of three phases, namely CsBr, Cs₄PbBr₆, and CsPbBr₃ (Fig. S5 in the ESM). It is worth mentioning that the spots of stronger contrast observed within the Cs-deficient particles (Fig. 1(e)) and pointing to the presence of Pb decompose during intense electron illumination; hence, these spots are not visible in the high-resolution TEM and HAADF-STEM micrographs as well as the element maps (Fig. 2). Based on the comparative analysis of the results provided by XRD and electron microscopy, we propose a possible mechanism of the formation and phase transformation of these particles during grinding, which is discussed below and schematically presented in Fig. 2(g) and Fig. S6 in the ESM.

After adding h-PMMA/PEI solved in DCM to the milling jar, most h-PMMA remains in the solvent phase of DCM; however, most PEI bounds quickly to PbBr₂ in the solid phase, which is expected considering the different binding forces between the corresponding polymer (h-PMMA or PEI) and the solid phase [36, 37]. The h-PMMA may form micellar templates for the growth of NPs due to the interactions between the hydrophobic ester bond and hydrophilic carboxylic acid group (or carboxylic acid anion) in the non-polar DCM. A possible formation of micelles in the polymer solutions in DCM was monitored by the Tyndall experiment and by dynamic light scattering (DLS) measurements (Fig. S7 in the ESM). The solution of conventional non-hydrolyzed PMMA appeared completely transparent for the laser beam. The obvious formation of scattering particles was evidenced in the DCM solutions of h-PMMA and h-PMMA/PEI. Moreover, the DLS results show a higher degree of aggregation of the polymeric phase upon the introduction of PEI; in other words, micelles of a bigger average size could be formed. Thus, the reason for the increase in particle size of the resulting NPs may partly be attributed to the fact that after PEI introduction the negatively charged carboxylate from h-PMMA causes assembling into larger micelles.

As the direct in situ observation of the micelles formed during the milling process is impossible and considering the influence of heat and uneven distribution of PEI on micelle assembly behavior in the milling reactor is cumbersome, the results of the Tyndall and DLS experiments can only provide indirect evidence for the origin of micelle formation. In addition, a control experiment of grinding exactly the same precursors in absence of h-PMMA was carried out. In this case, we failed to obtain the colloidal solution of perovskite NPs (Fig. S7(c) in...
the ESM). The resulting powder particles are in the size range of micrometers (Fig. S7(d) in the ESM), which is expected and consistent with literature reports [38, 39]. In its own turn, the nano-sized perovskite NPs can be prepared in the presence of h-PMMA as shown in Fig. 1(a). The analysis of the above measurements allow us to suggest that the uniform size of NPs prepared by grinding can be attributed to the h-PMMA micellar templates formed in DCM. The micellar fabrication of various nanocrystals is well known and was successfully applied to the synthesis of CsPbBr$_3$ by Yoon et al. [40, 41]. In those works, the authors used star-like PAA-b-PS nanoreactors to obtain monodisperse particles with solution-based synthesis.

The highly branched PEI, which is rich in amino-groups (about 600 amino groups per PEI-25K molecule), could form a complex with PbBr$_2$ in solid phase, due to the strong interaction between the vacant orbital from Pb$^{2+}$ and the lone electron pair of nitrogen from PEI [36, 37]. This complexation will further result in the redistribution of the material in the reaction mixture into the PbBr$_2$-rich phase of CsPbBr$_3$-xPbBr$_2$/PEI and the rest, i.e., the CsBr-rich phase of CsPbBr$_3$-yCsBr, in accordance to Reaction (1)

$$\text{CsPbBr}_3\text{(solid)} + \text{PEI} \rightarrow \text{CsPbBr}_3\text{-xPbBr}_2/\text{PEI (in solid)} + \text{CsPbBr}_3\text{-yCsBr (in solid)} \quad (1)$$

The values of $x$ and $y$ in Reaction (1) reflect an additive influence of both the molecular weight and the amount of PEI molecules. Thus, these values are expected to be relatively high if the high-molecular-weight PEI-25K is used as compared to the case when the low-molecular-weight PEI-0.8K was used, as we did in our previous report [36]. Of particular note, the value of $x$ should be significantly higher than the value of $y$, since PEI-25K can only enrich PbBr$_2$ but not CsBr. Both phases formed in Reaction (1) can undergo further transformations under the conditions considered here. The CsPbBr$_3$-xPbBr$_2$/PEI phase can further convert to CsPb$_2$Br$_5$-mPbBr$_2$/PEI based on Reaction (2)

$$\text{CsPbBr}_3\text{-xPbBr}_2/\text{PEI} \rightarrow \text{CsPb}_2\text{Br}_5\text{-mPbBr}_2/\text{PEI} \quad (2)$$

This phase conversion is well expected due to the low binding energy of perovskite materials. It is worth noting that if the molecular weight or amount of PEI added is very low, resulting in a small value of $x$, the final product of the reaction should be CsPb$_2$Br$_5$-Cs$_4$PbBr$_6$-nCsBr instead of CsPbBr$_3$-xPbBr$_2$/PEI, in accordance with our previous work [36]. The CsPbBr$_3$-yCsBr phase in its own turn can spontaneously be converted to CsPbBr$_3$-Cs$_4$PbBr$_6$-nCsBr based on Reaction (3)

$$\text{CsPbBr}_3\text{-yCsBr} \rightarrow \text{CsPbBr}_3\text{-Cs}_4\text{PbBr}_6\text{-nCsBr} \quad (3)$$

It should be noted that $m$ and $n$ used in Reactions (2) and (3), respectively, are parameters representing some arbitrary fraction of the coefficients $x$ and $y$ in Reaction (1), which are ultimately determined by the amount of PEI added and its molecular weight. Under high-speed shaking and milling, the above two products formed in Reactions (2) and (3) could enter into the solution to form colloidal particles coordinated with h-PMMA ligand through the interaction of carboxyl or carboxylate and Pb$^{2+}$, as illustrated in the diagram of Fig. 2(g). However, compared to CsPb$_2$Br$_5$-Cs$_4$PbBr$_6$-nCsBr particles, the particles of CsPb$_2$Br$_3$-mPbBr$_2$/PEI can provide more binding sites for the coordination with h-PMMA; therefore the product of

\[\text{CsPbBr}_3\text{-xPbBr}_2/\text{PEI} \rightarrow \text{CsPbBr}_3\text{-mPbBr}_2/\text{PEI} \quad (2)\]

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Reaction (2) will enter into solution with a higher rate and the NPs of CsPbBr3−mPbBr2/NPs coordinated with h-PMMA become a major colloidal product. On the other hand, a relatively small amount of CsPbBr3−CsPbBr−nCsBr NPs can enter into colloidal solution, which makes them a minor product of the reaction.

One more side reaction, which is necessary to complete the picture, should be mentioned here. PbBr2 available in the product of Reaction (2) can be reduced to Pb0 by amino groups of the PEI-25K under the heating caused by the high-speed milling [42, 43].

\[
\text{PEI-NH}_2 + \frac{1}{2}\text{PbBr}_2 \rightarrow \text{PEI-NH}_2\cdot\text{Br} + \frac{1}{2}\text{Pb}^0
\]

(4)

For simplicity, we normalized the reaction stoichiometry to a single amino-group. It is, however, clear that the highly branched PEI contains plenty of amino entities available for this reaction. We attribute the spots of a higher contrast material observable inside of the spherical nanoparticles in Fig. 1(e) to the metallic Pb formed in Reaction (4) [42, 43]. Diffraction peaks of neither Pb nor PbBr2 and CsPbBr5 phases can be recognized in powder XRD patterns (Fig. 1(g)). This observation may reflect the formation of amorphous phases or solely very small crystallites of these materials under conditions of binding to the polymer of high molecular weight and branched PEI-25K [44, 45].

The results of this part can thus be summarized as follows: if h-PMMA is the only ligand applied in the synthesis, the above-described phase conversions are not observable. The CsPbBr3 NPs in solid phase enter into DCM to become the only colloidal product after combination with h-PMMA. Therefore, the resultant NPs capped by h-PMMA show the perovskite phase, a cubic shape, and an element composition corresponding to CsPbBr3 (Figs. 1(a) and 1(g)). The introduction of PEI triggers the above-listed series of phase transition reactions resulting in the appearance of two colloidal products, namely the major amorphous product of CsPbBr3−mPbBr2 particles coordinated with PEI/h-PMMA and the minor crystalline product of CsPbBr3−CsPbBr−nCsBr particles coordinated with h-PMMA. Increasing the amount of the branched PEI added to the reaction causes the preferable formation of h-PMMA-capped CsPbBr3−mPbBr2/PEI NPs. This was reflected by the gradual increase in the elemental ratio of Pb and Br in the final product (Figs. 1(a)–1(f)).

2.3 Spectral characterization

The NPs obtained with different amounts of PEI (0, 0.01, 0.015, 0.020, 0.025, and 0.030 g) were characterized by optical spectroscopy. The NPs obtained with solely h-PMMA as ligand exhibit a typical absorption spectrum of CsPbBr3 NPs. Furthermore, they show a narrow PL with a FWHM of about 16 nm peaking at 518 nm with a QY of 8.2% (Fig. 3 and Table S2 in the ESM).

After the introduction of PEI-25K, the strong absorption peaks appearing at 290–320 nm indicate the occurrence of non-CsPbBr3 phases for the resulting NPs. This is accompanied by a slight blue shift of the PL maximum (about 2 nm) and the significant increase of the PL QY. Based on the phase conversion mechanism discussed above, it can be concluded that both Cs-rich and PbBr-rich particles could contribute to the PL, if the amount of PEI added to the system is relatively low (e.g., around 0.01 g). As followed from the Reaction (2), the PbBr-rich particles are expected to consist of CsPbBr3−CsPbBr−nCsBr with this amount of PEI. If the amount of PEI added is higher (i.e., 0.015 g or more), the PbBr-rich phase consists of CsPbBr3−mPbBr2 and could not contribute to the emission. In this case, solely the emission from the CsBr-rich NPs, namely the CsPbBr3−CsPbBr−nCsBr obtained according to the Reactions (1) and (3) is observed. The slight deviations in the PL positions may reflect the deviations in average particle sizes.

Moreover, the significant increase of the PL QYs should result from the wide energy bandgap of CsPbBr3 improving the carrier confinement in the CsPbBr3 phase and suppressing its surface defects [6, 28]. The optical absorption in the spectral region of 460–520 nm is associated with CsPbBr3 phase [34, 35]. Although, the absolute quantification of these data is complicated due to the uncertainty of the extinction coefficient of the NPs, the relative analysis is well applicable. Indeed, with increasing amount of the PEI-25K added to the synthesis, this absorption feature diminishes, indicating a decrease of the relative amount of CsPbBr3 phase (Fig. 3(a)). Thus, in order to obtain strongly emitting NPs, the amount of the PEI added to the system should be carefully optimized. In this work, the NPs modified by 0.025 g of PEI-25K were found to consist of a balanced amount of about 15% of CsPbBr3−CsPbBr−nCsBr fluorescent phase, allowing this sample to exhibit the highest PL QY of 85%. The fluorescence decay measurements show that, upon the introduction of PEI-25K, the fluorescence lifetime of the resulting NPs increases (from 8.4 to 15.0 ns) (Fig. 3(d) and Table S2 in the ESM). This may be the result of the combined effects of both the change in particle size of the CsPbBr3 phase and the passivation of the CsPbBr3 surface by the Cs4PbBr6 phase [28, 36].

To demonstrate the versatility of our approach and its applicability to obtain NPs with other emission colors, blue- and red-emitting NPs were prepared by ion-exchange reactions. To this end, the NPs prepared with 0.025 g of PEI-25K were treated with ZnCl2 and ZnI2 dissolved in CH3OH, respectively. True-color images, absorption and PL spectra of the resulting NPs are shown in Fig. S8 in the ESM, and the corresponding spectral data are summarized in Table S3 in the ESM. The deep blue-emitting NPs exhibit a PL peak at 456 nm, a narrow FWHM of ~ 12.9 nm, and a PL QY of 28%, while the red-emitting NPs are characterized by a PL peak at 641 nm with a larger FWHM of ~ 38.6 nm and a PL QY of 32%. The decrease in the PL QY after ion exchange is consistent with

![Figure 3](image-url)
previously reported works [46, 47], which may be due to relatively poor defect tolerance of the chloride-based and iodine-based perovskites [12].

2.4 Stability and durability during solution-based processing

Our previous work indicated that the dual-ligand system of h-PMMA and PEI significantly improves the water resistance, thermal and UV stability of perovskite materials [36]. In the present work, we extended these investigations to the stability in polar solvents and the durability during the precipitation/redispersion steps. Such kind of treatments are typical, if a colloidal material is subjected to solution-processing technologies (e.g., spin- or dip-coating, casting, spraying or ink-jet printing). Because of the ionic nature of perovskites and their weak-binding to OLA/OA, a strong-polarity solvent, such as methanol or ethanol, can cause the decomposition of perovskite NPs and a substantial loss of the capping ligands accompanied by the complete quenching of the PL [14, 15]. However, the NPs prepared and stabilized by polymer show a high resistance to methanol (Figs. 4(a) and 4(b)). The NP solutions still maintain 65% of their original PL intensity after replacing half of the toluene solvent with methanol (Fig. 4(b)). The fluorescence intensity of the resulting methanol-containing NP solutions was reasonably stable during at least seven days of storage (Fig. S9 in the ESM). This high degradation resistance is provided by the protective layer formed by the hydrophobic PMMA [48], whereas the partial deterioriation of the PL may be caused by the weakening of the coordination ability of the PEI in methanol. For OA/OA-coordinated perovskite NPs, it is common to use polar solvents, such as acetone and n-butanol in combination with high-speed centrifugation to precipitate them. This procedure is applied for “washing” colloidal particles, changing solvent, or increasing their concentration and is often accompanied by the loss of capping OLA, which in turn causes a significant decrease in the PL QY (Fig. 4(c)). Since h-PMMA impart the NPs an obviously different level of solubility as compared to OLA/OA-capped NPs, the former particles can be precipitated without using polar solvents and high-speed centrifugation. The destabilization of the colloidal solution may be achieved in this case by the addition of another non-polar solvent, e.g., n-hexane. More importantly, such a simple method of NP-concentrating is also very robust in that it does not lead to a decrease in PL QY (Figs. 4(c) and 4(d)). After seven times of precipitation with n-hexane and dispersion in toluene, the PL QY of the NPs coordinated by polymer hardly changes as shown in Fig. 4(c). For comparison, regular OLA/OA-capped strongly emitting perovskite NPs were prepared according to the literature [14, 15], and their PL QY was monitored after each cycle of precipitation/redispersion with the polar solvent ethyl acetate. The PL QY of this reference sample decreases from the original 85% to 10% at the end of the 7th precipitation step, owing most likely to the loss of the weakly-binding OLA. The NP-polymer precipitates obtained here exhibit excellent processability imparted by the polymer-ligand. The NP-polymer film appears transparent and greenish, due to the strong PL, which is visible even under ambient light. The samples are also strongly luminescent under UV excitation (Figs. 4(d) and 4(e)). Predictably, the NP-polymer films show excellent storage stability due to the water-resistance of PMMA.

2.5 Amplified spontaneous emission

The h-PMMA/PEI-capped NPs exhibit a high PL QY, excellent stability, and good processability, all together making them attractive for optical applications, especially for solution-based processing. Here, we demonstrate ASE to show the capability of these NPs to be used for lasing. The ASE can be readily achieved from the h-PMMA/PEI-capped NPs film under femtosecond laser excitation at 400 nm (see Experimental Section). The dynamics of optical gain in the PMMA/PEI-capped NPs film was measured under stripe excitation geometry [49].

As the pump fluence is increased, a second emission feature emerges, which is attributed to ASE (Fig. 5(a)), as evident by its much narrower FWHM (~ 6.2 nm) at room temperature in comparison to that of the spontaneous emission feature (~ 17 nm) as well as a superlinear increase in the output intensity (Fig. 5(b)). The ASE peak is red-shifted by 16 nm with respect to the spontaneous emission peak, suggesting attractive multieexcitonic interaction within these NPs. The emission intensity versus the pumping fluence is plotted in Fig. 5(b), from which an ASE threshold of 18.9 μJ/cm² can be extracted. In addition, the pump-dependent gain coefficient for the sample has been determined via the variable stripe length technique [49, 50] at various pump intensities. Figure 5(c) shows the emission intensity at the ASE peak wavelength (~ 534 nm) for various stripe lengths. Accordingly, for a homogeneously excited stripe of length l, the total emission is given by Eq. (5)

\[ I = \frac{I_0}{g} (e^{gs} - 1) \]  

where \( I_0 \) is the spontaneous emission constant. The net gain coefficients extracted from the data in Fig. 5(c) are presented in Fig. 5(d) as a function the of the pump fluence. The net gain coefficient can be expressed as

\[ g = A \frac{W_e}{W_p + W_s} - \alpha \]  

where A is a constant proportional to the stimulated emission cross-section, \( W_e \) is the excitation pump intensity, \( W_s \) is the saturation pump intensity, and \( \alpha \) is the loss coefficient. The data in Fig. 5(d) are seen to fit well to Eq. (6). We therefore determine the saturation intensity to be \( W_s = 73.5 \, \mu J/cm^2 \) and...
phases. The obtained CsPbBr$_3$-Cs$_4$PbBr$_6$- 

Figure 5  ASE of h-PMMA/PEI-capped NPs film. (a) Emission spectra of h-PMMA/PEI NPs film with increasing excitation fluence. (b) Integrated emission intensity (blue circles) and FWHMs of the emission spectra (red triangles) as a function of the pump energy density. (c) Variable stripe length (VSL) measurements on the h-PMMA/PEI-capped NPs film. PL intensity at the ASE peak (534 nm) as a function of the stripe length for different pump fluences. (d) Extracted net gain coefficients from the data in panel (c). From the fitting in Eq. (6), the saturation intensity is found to be 73.6 μJ/cm$^2$ and the loss coefficient ~ 110 cm. The net saturated gain is ~ 425 cm$^{-1}$ (dashed line).

the loss coefficient to $\alpha = 110$ cm$^{-1}$. The net gain coefficient asymptotically approaches to 425 cm$^{-1}$, which is thus determined as the saturated gain coefficient.

We note that the ASE threshold achieved by the resulting PMMA/PEI-capped NPs film is lower than previous results reported in the literature [51]. Furthermore, ASE is observed only for the samples with a high-enough density of NPs. In this respect, the polymer ligands inevitably introduce separation between individual NPs, thereby reducing their density, which might be limiting the optical gain coefficient and increasing the gain threshold. This means that our gain medium made of these NPs can potentially be further optimized by tuning the composition, molecular weight, and amount of polymers used for the capping in order to control the inter-particle distance. The successful demonstration of ASE in this work shows that our PMMA/h-PEI-capped NPs possess a great potential as stable and processable luminescent materials in such optical gain media.

3 Conclusion

High molecular weight PEI-25K and h-PMMA were used as double ligands in the preparation of perovskite NPs by milling. The roles of h-PMMA and PEI-25K in the milling process were studied in depth. The h-PMMA forms micelles in DCM to act as templates for uniform NP growth, whereas high-molecular-weight PEI-25K induces significant enrichment of PbBr$_2$ during the milling process, which in turn causes the formation of CsPbBr$_3$-nPbBr$_2$ and CsPbBr$_3$-CsPbBr$_3$-nCsBr phases. The obtained CsPbBr$_3$-Cs$_4$PbBr$_6$-nCsBr NPs are responsible for the high PL QY of the resulting NP-polymer solutions and solid composites, since the Cs$_4$PbBr$_6$ phase with a wide band gap energy can passivate the surface defects of the emitting CsPbBr$_3$ phase. The as-prepared NPs solutions exhibit a wide band gap energy can passivate the surface defects of the resulting NP solutions possess excellent durability and resistance to methanol as well as offer solution-based processability, making them attractive as solution-processable optical gain media. This work provides new insights in the preparation of uniformly sized perovskite nanoparticles by grinding and sheds light on the mechanism of a phase conversion happening with such perovskite materials under grinding and influence of an amino-group rich medium.

4 Experimental section

4.1 Preparation of perovskite nanoparticles

PMMA possessing a degree of hydrolysis of 10% (h-PMMA) was prepared based on our previous work [36]. The perovskite NPs were prepared by mechanical grinding as follows. PbBr$_2$ (73.4 mg, 0.2 mmol) and CsBr (42.4 mg, 0.2 mmol) were loaded under ambient atmosphere into a zirconia bowl (10 mL) with about 3 mL of zirconia balls (2 mm in diameter) and mixed by a vibratory mill MM 400 (Retsch). The first grinding process of the educts lasted 30 min at a frequency of 30 Hz. Next, 0.1 g of h-PMMA and different amounts (0, 0.01, 0.015, 0.02, 0.025, and 0.03 g) of PEI-25K were dissolved in 5 mL of DCM and added to the milling jar. The milling process was continued for another 30 min resulting in the formation of the NPs. Next, the mixture was diluted with 5 mL of DCM and centrifuged for 5 min at 5,000 rpm. The supernatant containing the NPs was collected, and the NPs were destabilized by adding n-hexane. The resulting suspension was centrifuged at 5,000 rpm for 5 min. The precipitate was re-dissolved in 10 mL of toluene for further characterization and processing. For anion exchange, 0.1 M solutions of ZnCl$_2$, or ZnI$_2$, in CH$_2$OH$_2$ were used to treat the original h-PMMA/PEI-stabilized green-emitting NPs. The OLA/OA-coordinated CsPbBr$_3$ NPs (as a reference sample for the stability test) were prepared by the hot injection method in exact accordance with the literature [52, 53].

4.2 Centrifugal purification of perovskite nanoparticles

High-speed centrifugation could be used to additionally purify the NPs. Specifically, the as-prepared NPs in toluene were centrifuged at 10,000 rpm for 5 min to collect supernatant. The excessive polymer was removed by further high-speed centrifugation with 13,000 rpm for 15 min. The precipitate was collected and re-dissolved in pure toluene.

4.3 Test of anti-methanol stability and durability

An equal volume of methanol was added to the toluene solution of NPs to test its stability against polar solvents. For PL measurements, the NPs solution in the control group was directly diluted twice with toluene. For the durability test of the NPs capped by h-PMMA/PEI, excessive n-hexane was used to precipitate the NPs dissolved in toluene. The precipitate was re-dispersed into the same amount of toluene as initially used. The above precipitation/redispersion steps were repeated several times. For testing the durability of OLA/OA-capped NPs, a 3-fold volume of ethyl acetate was added to the toluene solution to precipitate the NPs, followed by centrifugation at 10,000 rpm for 5 min. The precipitate was re-dispersed into the same amount of toluene as initially used. The above precipitation/redispersion steps were repeated several times.

4.4 Optical gain measurements

Before preparing the NP films for the ASE testing, excess polymer in the resulting h-PMMA/PEI-capped NPs was removed based on the above purification steps. After purification and
high-speed centrifugation, the precipitate was dissolved in a small amount of toluene and then deposited on quartz glass (1 cm × 1 cm) to obtain a film with a high density of emitting NPs. For ASE measurements, we used pulses from a Ti:Sapphire laser amplifier (Spitfire, Spectra Physics) with a pulse width of ~110 fs at a pulse rate of 1 kHz and 800 nm wavelength. The wavelength was halved with a frequency-doubling nonlinear crystal, and the remaining 800 nm excitation was filtered out via a short-pass filter. The incoming 400 nm pulses were passed through a cylindrical lens to obtain a stripe excitation. The sample was positioned at the focal point of the cylindrical lens and oriented normally to the pump. The emission was collected from the edge of the sample with an optical fiber coupled to a spectrometer (Meya 2000, Ocean Optics). For VSL measurement, a slit with variable width was placed right before the sample to control the length of the excitation stripe.

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