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Highly stable, luminescent core–shell type methylammonium–octylammonium lead bromide layered perovskite nanoparticles†

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A new protocol for the synthesis of a highly stable (over 2 months under ambient conditions) solution-processed core–shell type structure of mixed methylammonium–octylammonium lead bromide perovskite nanoparticles (5–12 nm), having spherical shape, color tunability in the blue to green spectral region (438–521 nm) and a high photoluminescence quantum yield (PLQY) of up to 92% is described. The color tunability, high PLQY and stability are due to the quantum confinement imparted by the crystal engineering associated with core–shell nanoparticle formation during growth.

Organic–inorganic hybrid halide perovskite materials have already revolutionized solar cell applications.^{1–6} The certified power conversion efficiency of solar cells based on CH₃NH₃PbI₃ and derivatives have reached a record value of 20.8% within a short period.⁶ Concurrently, the potential of perovskites to transform the field of light emission has been demonstrated.^{7–11} The focus has now been expanded to encompass the fabrication of perovskite nanoparticles (NPs) to achieve color tunability and enhanced PLQYs. It appears that even a slight change in the synthetic protocol can significantly influence the band-gap tuning, size, ordering and photophysical properties of the NPs.^{12–15} For example, the Perez-Prieto group reported a non-template strategy for the synthesis of colloidal methylammonium lead bromide (MAPbBr₃) NPs with a particle size of around 6 nm showing a photoluminescence quantum yield (PLQY) of up to 83%,¹⁶ whereas the Dong group reported a ligand-assisted reprecipitation strategy (LARP) for the synthesis of MAPbBr₃ NPs with a particle size of around 3.3 nm and photoluminescence quantum yield (PLQY)

between 50 and 93%.^{14,17} Despite these promising results, efforts have not been made to improve luminescence stability in parallel with enhancing the PL efficiency.

One of the methods to enhance the stability, efficiency and brightness of semiconductor nanocrystals is by growing a shell of a larger band-gap semiconductor around it.^{12,18} Such NPs with small regions of one material embedded in another with a wider band gap are known as core–shell semiconducting nano-crystals (CSSNCs). This type of crystal engineering improves the quantum yield of the NPs by confining charge carriers, passivating non-radiative recombination sites and making them more robust to processing conditions. In a bid to explore the same advantages in perovskite NPs, we have investigated the possibility of developing NPs comprising of a high band-gap 2D perovskite (C₈H₁₇NH₃)₂(CH₃NH₃)_{n-1}Pb_nBr_{3n+1} (*n* = 1, 2, 3,...) shell over a low band-gap MAPbBr₃ core as shown in Fig. 1a.

The LARP method was adopted for the synthesis.¹⁷ Methylammonium bromide, lead bromide, oleylamine and oleic acid were dissolved in DMF in an appropriate molar ratio to make the final precursor solution for MAPbBr₃ NPs (ESI†). 250 mL of this precursor solution was then swiftly injected into 5 mL of toluene kept at 60 °C and stirred vigorously for 5 min to form MAPbBr₃ NPs. The mixture was then centrifuged and the supernatant containing the NPs was collected for further studies. For the synthesis of the mixed cation MA–OA lead bromide NPs, MABr and OABr at 8:2, 6:4, 4:6, 3:7 and 2:8 molar ratios were used in the precursor solution such that the total amount of organic ammonium bromide and synthesis conditions are constant for all combinations. The structural characterization of the NPs thus prepared were done using transmission electron microscopy (TEM) and X-ray powder diffraction (XRD) and their photophysical properties were evaluated by recording their optical absorption, photoluminescence (PL) and time resolved photoluminescence spectra.

Fig. 1b and c show representative TEM images of spherical mixed organo-lead bromide NPs obtained from cation ratios 8 : 2 and 3 : 7 (see the ESI† for all combinations of cations).

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Fig. 1 (a) Schematics showing the core-shell type layer growth of octyl-ammonium lead bromide nanomaterials over MAPbBr₃ NPs. (b and c) TEM images of core-shell NPs with MABr and OABr molar ratios 8 : 2 and 3 : 7 respectively. (d–f) Photographic images of mixed organolead bromide perovskite NPs with different MABr–OABr ratios in toluene solution under UV exposure over different time intervals.

The NPs seem to be spherical with an average diameter of 5–12 nm. There is no signature of the formation of 3D bulk crystals or platelets. This may be due to the influence of the oleylamine used as a capping ligand in this synthesis which controls the growth and crystallization of NPs whereas oleic acid prevents NPs from self-aggregation and at the same time contributes to the colloidal stability.¹⁷ No significant size change was observed for the particles obtained with cation ratios 8 : 2 and 6 : 4 (particle size B5 nm) whereas synthesis with cation ratios 3 : 7 and 2 : 8 afforded NPs with a particle size of around 12 nm. The as-synthesized particles showed bright luminescence under UV light (Fig. 1d–f). Remarkably, the luminescence of certain compositions (stored under ambient conditions, at 60% RH) remained stable for 2 months. Specifically, the mixed compositions within a limited MABr : OABr range remained highly luminescent. This indicated the possible advantages brought about by the core-shell architectures and motivated further analysis.

We evaluated the photophysical properties of these core-shell NPs. The optical absorption of the pure MAPbBr₃ ($n = N$) NPs (Fig. 2a) showed an absorption maximum centered at 513 nm. This absorption peak is blue shifted by 12 nm compared to that reported for the bulk materials (band-gap = 2.3 eV or 525 nm).^{19,20} This points to three dimensional confinements in the system possibly due to the formation of nano-sized spherical MAPbBr₃ particles. The absorption shift for precursor solutions with an OABr content of 40% was not significant. Perovskites with a higher OABr concentration displayed a large blue shift for the absorption maxima as well as the formation of additional absorption peaks.

Fig. 2 (a) UV-vis absorption and (b) PL spectra of mixed organo-lead bromide perovskite NPs with different molar ratios of MABr and OABr.

For example, perovskite with MABr : OABr = 4 : 6 showed absorption peaks at 397, 433, 450, 471 and 486 nm which are typical for layered perovskites with $n = 1, 2, 3$ or higher order, respectively as shown in Fig. 4a.^{19,21–23} A similar trend is observed for perovskites formed with MABr : OABr = 3 : 7 and 2 : 8 (see Table S1 in the ESI†).

Subsequently the photoluminescence properties of these materials were studied. As shown in Fig. 2b, the MAPbBr₃ NPs showed green emission with a PL peak position centered at 521 nm (FWHM = 24 nm) and a PLQY of around 80–84%. The mixed cation MABr–OABr (8 : 2) NPs showed a slight blue shift in the PL peak position (519 nm) with an enhanced PLQY of 92%. This material showed unusual stability in solution in an ambient atmosphere; even after two months the PLQY remains virtually unchanged (see Table S3 in the ESI†). At a higher MABr : OABr ratio ($>4 : 6$), similar to the trend observed in the optical absorption, PL peak positions shifted to lower wavelengths and a concurrent decrease in the PLQY was observed (see Table S1 in the ESI†). In addition, perovskites with MABr : OABr = 4 : 6 and 3 : 7 showed three PL peak positions, whereas the 2 : 8 composition showed only two PL peak positions.

Generally, the organic–inorganic perovskite structure (AMX₃) is formed by a three dimensional network with small organic cations occupying the A-site, and divalent metal and halides forming the MX₆ octahedra. The peak positions observed for the MAPbBr₃ NPs (Fig. 3a) match well with the patterns reported for bulk crystals,²⁰ with a d -spacing of 5.9 Å. However, if larger cations (>2.6 Å) are introduced,²⁴ the cubic symmetry is broken; instead layered structures of the general formula (RNH₃)₂A _{$n-1$} M _{n} X_{3 $n+1$}

Fig. 3 (a–d) XRD pattern of mixed organolead bromide perovskite NPs with different MABr and OABr molar ratios. Inset of (b–d) shows a magnified view of the corresponding XRD pattern.

($n = 1$, pure 2D layered; $n = N$, 3D structure; and n = defined integer, quasi-2D layered structure) are formed. The diffraction pattern of 8 : 2 NPs (Fig. 3b) show additional peaks at lower diffraction angles, originating from layered structures, along with peaks associated with 3D perovskite formation. Although the (100) and (200) peak intensities are lower for the 8 : 2 NPs compared to 10 : 0, the relative intensity difference and peak positions remain unchanged.

In 2D layered perovskites like $(\text{OA})_2\text{PbBr}_4$, the inorganic lead halide layers are separated by the large organic cations (*i.e.* large d -spacing). In order to explain the d -spacing values observed in the XRD patterns of the mixed NPs, we recorded the XRD pattern of pure layered $(\text{OA})_2\text{PbBr}_4$ ($n = 1$) prepared by a previously reported method (see the ESI†).²⁵ This layered compound showed a d -spacing of approximately 10.5 Å. In this case the two dimensional $[\text{PbBr}_6]^{4-}$ layers are separated by n -octylamine ligands. Knowing the exact d -spacings for the MAPbBr_3 and $(\text{OA})_2\text{PbBr}_4$, it is possible to conduct a basic elucidation of the varied d -spacings noted in the mixed NPs (without taking strain/solvation effects into consideration). In the XRD patterns of 3:7 and 2:8 NPs (Fig. 3c and d), the peaks observed at lower diffraction angles correspond well to the expected positions for 2D perovskite layers. For MABr : OABr = 3 : 7, the observed d -spacing values are 10.31, 15.43, 18.7 and 21.4 Å. Similarly, for MABr : OABr = 2 : 8 the observed d -spacing values are 13.69, 15.27, 18.7, and 20.5 Å. The d -spacing of 13.69 Å most likely corresponds to a different layered phase or a different interlayer arrangement of OABr (see the ESI†).

The varied d -spacings point to the co-crystallization tendency of the organic ammonium perovskites. The high PLQY and stability of the 8 : 2 NPs could possibly be explained by the formation of such a mixed organic shell. The clear 519 nm PL signature of the NPs indicates that the main emitting species is MAPbBr_3 . However the weak optical absorption signature at 433 nm points to the possibility of a $n = 2$ shell.²¹ Such a higher band-gap shell would allow for efficient confinement and also impart stability. We believe that the observed PLQY and

stability enhancement, in combination with the blue-shift in the 8 : 2 sample originate from the formation of a core–shell type structure, in which the core consists of MAPbBr_3 and the shell of layered $(\text{OA})_2\text{PbBr}_4$. However, due to the low electron density contrast between the core and the shell, and the structural instability at high magnification, no direct evidence of its formation could be presented using HRTEM. Instead, its formation is rationalized *via* a series of indirect observations from additional experiments (for full details and explanations, see the ESI†). For example, replacement of the oleylamine ligand with octylamine for MABr : OABr = 10 : 0 resulted in a significantly lower PLQY and a red-shift in PL (see Tables S1 and S4, ESI†), whereas a similar blue-shift is observed for the 8 : 2 samples. This implies that OABr is the predominant factor to form a layered perovskite. In order to explore whether the 433 nm signature originates from $(\text{OA})_2\text{MAPb}_2\text{Br}_7$ ($n = 2$), we attempted to synthesize spherical $(\text{OA})_2\text{PbBr}_4$ NPs using the LARP method without the addition of MABr; the failure to produce the expected NPs suggests that a 3D MAPbBr_3 core is essential for the subsequent growth of 2D layers.

Experiments with OA-Br addition after the formation of MAPbBr_3 NP seeds (equivalent to MABr: OABr = 8 : 2 and 2 : 8), resulted in green-emitting NPs with a PL maximum at 522 nm, instead of 519 nm and 438/451 nm, respectively. This further suggests, that only during coprecipitation of MABr and OABr in the presence PbBr_2 core–shell type nanoparticles are formed (see the ESI†). Thermogravimetric analysis provided additional evidence of a structural difference between MABr: OABr 10: 0 and 8 : 2 NPs; both organic components are released at a higher temperature in the 8 : 2 NPs than the 10:0 NPs, suggesting that additional energy is required to remove intercalated OA-Br from the layered shell (see the ESI†).

To further understand the PLQY-variation in the mixed organolead bromide NPs, the PL decay kinetics of these NPs were investigated (Fig. 4). The decay curves were fitted with exponential decay functions (the fitted lifetimes and amplitude weighted average lifetimes are provided in the ESI†). For the perovskite samples with MABr: OABr = 10: 0 and 8 : 2, the decays are nearly single-exponential. Their high PLQY, together with

Fig. 4 Time-resolved PL decay and fitted curves for mixed organolead bromide perovskite NPs in solution extracted at their dominant emission peaks (as shown in brackets) following excitation at 400 nm (1 kHz, 150 fs, 0.2 mJ cm⁻²). Solid lines are fitted curves.

the mono-exponential kinetics indicates that the recombination originates predominantly from the radiative exciton decay channels in these NPs. Based on the mono-exponential PL lifetimes (τ_{PL}), the non-radiative recombination lifetimes ($\tau_{\text{non-rad}}$) can be estimated using $\tau_{\text{non-rad}} = \tau_{\text{PL}} / (1 - \phi_{\text{PL}})$, where ϕ_{PL} is the PLQY. The $\tau_{\text{non-rad}}$ in the MABr: OABr = 10 : 0 and 8 : 2 samples are 173 and 135 ns, respectively. The longer $\tau_{\text{non-rad}}$ in the latter clearly shows a better suppression of the non-radiative channels through improved surface passivation afforded by the growth of the outer shell. On the other hand, for the perovskite NPs with 6 : 4 to 2 : 8 MABr : OABr ratios, their transient PL (at their main emission peak) exhibits bi-exponential decay kinetics, with a dominant short (few ns) lifetime component and a longer lifetime (10–20 ns). Nonetheless, the amplitude-weighted average exciton lifetime reveals a shortened value ranging from 4.2 to 8.5 ns for these samples (see Table S2 in the ESI†). The faster decay stems from the presence of non-radiative channels associated with increased defects and surface traps, possibly due to the presence of more 2D perovskite layers, thereby resulting in a lower PLQY for the higher OABr concentrations.

Finally the PL stability of our mixed organolead bromide perovskite NPs was examined (stored under ambient conditions, at 60% RH). The photographs in Fig. 1d–f show the PL emission under UV exposure at different time intervals. The initially observed 84% PLQY for MAPbBr₃ NPs showed a considerable decrease with time and reached a value of 45% after one month and totally quenched after two months (see Table S3, ESI†). Interestingly, the initially observed 92% PLQY for MABr: OABr = 8 : 2 was found to be more stable and showed only a slight decrease with time and reached a value of 85% after one month and 60% after two months. The 82% PLQY observed for perovskite NPs with 40% OABr reduced to 60% after one month and 20% after two months. Perovskite NPs with a higher amount of OABr showed a fast decay of PL intensity with the increase in time. This may be due to the increase in the lattice strain caused by the increase in the 2D shell thickness.¹⁸

In conclusion, we have developed a new protocol for the synthesis of solution-processed, highly stable and color tunable core–shell type mixed methylammonium–octylammonium lead bromide perovskite NPs with a spherical shape and a high PLQY. The cation ratio in the precursor solution is the key factor controlling the layer growth, PLQY and stability of these mixed perovskite NPs. To the best of our knowledge, this is the first successful development of perovskite–perovskite core–shell type NPs. We hope that this study will open new avenues for the cost effective development of air stable and color tunable perovskite LEDs.

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