Monodisperse Formamidinium Lead Bromide Nanocrystals with Bright and Stable Green Photoluminescence

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Supporting Information

ABSTRACT: Bright green emitters with adjustable photoluminescence (PL) maxima in the range of 530–535 nm and full-width at half-maxima (fwhm) of <25 nm are particularly desirable for applications in television displays and related technologies. Toward this goal, we have developed a facile synthesis of highly monodisperse, cubic-shaped formamidinium lead bromide nanocrystals (FAPbBr3 NCs) with perovskite crystal structure, tunable PL in the range of 470–540 nm by adjusting the nanocrystal size (5–12 nm), high quantum yield (QY) of up to 85% and PL fwhm of <22 nm. High QYs are also retained in films of FAPbBr3 NCs. In addition, these films exhibit low thresholds of 14 ± 2 μJ cm−2 for amplified spontaneous emission.

In the last several years, lead halide semiconductors with perovskite crystal structures have emerged as very popular optoelectronic materials, initially in the context of highly efficient photovoltaics with power conversion efficiencies exceeding 22%1 and as versatile photonic sources. In particular, devices.4b,6 In the near future, the technologically most feasible high PL quantum yields (QYs = 50−90%)2 for amplification of spontaneous emission.

First of all, both the PL peak and absorption edge from CsPbBr3 NCs do not exceed 520 nm, even at NC sizes far beyond the quantum-confinement regime (>10 nm). This is indicative of the fact that the “apparent bulk bandgap” of CsPbBr3 NCs is higher than that obtained with large single crystals (with a band gap of 2.25 eV at, e.g., 551 nm).7 At present, the atomistic origin of this difference is unclear. The broad X-ray diffraction (XRD) reflections of CsPbBr3 NCs make it difficult to differentiate between the orthorhombic (nearly cubic) lattice of the bulk material and other possible distortions of the ideal cubic lattice. The PL maxima can be pushed to the desired 530–535 nm wavelengths compositionally, by forming CsPbBr3−xIx (x ≈ 0.3). However, this shift is accompanied by a drop of QY from 90 to ≤50%. Furthermore, CsPbBr3−xIx NCs exhibit low chemical stability in the solid-state, presumably due to phase-separation into CsPbBr3 and CsPbI3. Considerable attention has also been devoted to hybrid perovskites, methylammonium lead halides (MAPbX3), in the form of colloidal NCs.8 A particular challenge facing MA-based compounds is their chemical decomposition, releasing gaseous methylamine.

In this work, we explored a closely related compound FAPbBr3, where FA+ stands for CH(NH2)2+ (formamidinium). We present a colloidal synthesis of FAPbBr3 NCs and strong evidence that these NCs may overcome the difficulties facing CsPbBr3 NCs in achieving bright and stable emission at 530–535 nm. In a typical hot-injection synthesis (method 1, see Supporting Information for further details), FA-Pb precursor solution was prepared by reacting Pb and FA acetates (0.2 and 0.75 mmol, respectively) with oleic acid (OA, 2 mL) in octadecene (ODE, 8 mL). At 130 °C, oleylamine bromide (OAmBr, 0.6 mmol, dissolved in 2 mL of toluene) was injected. After 10 s, the FAPbBr3 NCs were cooled to room temperature and purified using toluene and acetoniitrile as a solvent and nonsolvent, respectively. This simple synthesis yields brightly luminescent, cubic-shaped and highly monodisperse FAPbBr3 NCs (Figure 1), with standard size deviation below 5% (Figure S1).

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The excellent PL properties of FAPbBr₃ NCs are exemplified by those of 12 nm in size, which exhibit a PL maximum at 530 nm, QY of 85% and fwhm of 22 nm (Figure 1b). The PL can be tuned in a wide range from 470 to 535 nm via size effects alone, without altering the composition. With NC sizes of up to 50 nm (Figure S2), PL peak values of up to 550 nm can be achieved, similar to the range reported for thin-film and bulk FAPbBr₃ (550–575 nm).3,4 Size-engineering was accomplished by adjusting either the amount of OAmBr injected (a higher quantity leads to smaller NCs, Figure S3) or the reaction temperature (between 70 and 165 °C, higher yielding larger size). We note that this synthesis (method 1) is significantly different from our previous work on CsPbBr₃ NCs, where PbBr₂ (dissolved in oleylamine, OLA, and OA) was used as a Pb–Br dual-source precursor.2 Such a CsPbBr₃-like synthesis of FAPbBr₃ NCs (method 2, see Supporting Information for details), which is by injection of FA-oleate precursor into PbBr₂/oleylamine/oleic acid mixture, yields a much broader size distribution of the NCs (Figure S4) than method 1. We attribute this to the detrimental role of molecular OLA, presumably causing deprotonation of FA+. Likewise, no FAPbBr₃ NCs could be obtained also when neutral OLA is introduced into method 1. An alternative Br-precursor, CH₃MgBr, has also been tested (method 3, see Supporting Information for details), leading to even faster reaction kinetics and thus poorer control over the NC size (Figure S5) than with OAmBr precursor. The complete absence of OLA or OAm+ led to lower colloidal stability, reinforcing the OAmBr-based method 1 as, thus far, the optimal synthesis route. Besides acting as the Br source, OAmBr also brings the OAm+ cation that together with the oleate-anion acts as capping ligands at the NC surfaces, presumably similarly to the CsPbBr₃ system.4,4b Oleylammmonium oleate is the sole byproduct of the synthesis (method 1) and a capping ligand at the same time, with oleate coordinating surface cations and OAm+ binding to surface anions. It is essential that the FA: Pb molar ratio is maintained above 2 in order to obtain stable luminescence materials. For FA:Pb ratios lower than 2, the obtained NCs rapidly decomposed. In contrast, CsPbBr₃ NCs require a high excess of Pb for optimal growth.2,5g

XRD studies on FAPbBr₃ NCs in thin films (Figure S6, laboratory data) and in solutions (Figure 2, synchrotron data) indicated the same primitive cubic structure (space group Pm₃m, no. 221) reported for bulk crystals, with a small, but measurable, increase of the unit cell parameter with respect to bulk (6.002 vs 5.992 Å).9 In FAPbBr₃, the PbBr₆ octahedra share their corners and the Br anions are disordered in four equivalent positions; consequently, the Pb–Br–Pb and cis-Br–Pb–Br bond angles appear to deviate from their ideal values of 180° and 90°, respectively, by up to 15°. As the slight reorientation of the PbBr₆ octahedra is likely to occur as rigid-body rotations, of the 24 disordered Br ions surrounding a central Pb atom, only 6 coherently de projected by the FA-Pb–oleate anion. This finding implies a severe conditioning of the connectivity pattern of the neighboring octahedron, which cannot be considered cubic at the very local scale, but only on average. With the aim of explaining the chemical reason for such a deviation from linearity, it has been recently proposed that the tilting of the PbBr₆ octahedra leads to a higher degree of space filling and, therefore, to a larger stability of the crystal structure.11 A careful analysis of the

Figure 1. (a) Photograph of colloidal FAPbBr₃ NCs in toluene solution under a UV lamp (λ = 365 nm), (b) absorption and PL spectra of ~12 nm FAPbBr₃ NCs with a PL maximum at 530 nm, fwhm of 22 nm and QY of 85%, (c) PL spectra for FAPbBr₃ NCs showing the red shift of the emission peak with increasing size from 5 to >50 nm, (d,e) TEM images of ~12 nm FAPbBr₃ NCs.

Figure 2. Synchrotron XRD pattern (λ = 0.565 666 Å) and its Rietveld fit for ~12 nm FAPbBr₃ NCs, containing an impurity of NH₄PbBr₅ (~6 wt %). Black, experimental data; green, calculated total trace that combines Pm₃m model of FAPbBr₃ and the I4/mcm model of NH₄PbBr₅.9,10 red, difference plot; black and magenta vertical bars indicate Bragg peak locations for FAPbBr₃ and NH₄PbBr₅, respectively. Stars highlight minor peaks of an unknown contaminant. The inset illustrates the crystal structure of FAPbBr₃ and disorder of Br-anions.
Contrary to conventional quantum dots, such as CdSe and InP, NCs, perovskite NCs feature unusual, defect-tolerant photo-contraction. The longer-living component (40 ns) that can be attributed to increased exciton delocalization. The longer-living component has not been observed in the closely related CsPbBr3 NC system.2 FAPbBr3 NCs show two characteristic lifetimes: one similar to the corresponding colloidal solution and a second, longer component of 60–70 ns, respectively. Such a size effect can be attributed to the higher exciton binding energy in such small crystallites due to quantum confinement. The QYs for both NC sizes were >70%. Contrary to conventional quantum dots, such as CdSe and InP NCs, perovskite NCs feature unusual, defect-tolerant photophysics,13 i.e., surface dangling bonds and intrinsic point defects such as vacancies do not form a high density of midgap states, known to trap carriers and thereby quench PL. CdSe and InP NCs, being defect-intolerant, require epitaxial passivation layers to exhibit bright PL. TR-PL traces from MAPbBr3 NCs quickly decomposed. The PL properties and exciton delocalization may assist in achieving lasing from FAPbBr3 NC emitters.5a

On the basis of our experience with CsPbBr3 and MAPbBr3 NCs,2,6 the only alternatives within the APbBr3 family, we find FAPbBr3 to be much more robust in several regards. When an identical, repetitive precipitation/redispersion procedure (with acetonitrile/toluene) is applied to any of the APbBr3 NCs, only FAPbBr3 can retain bright PL after 2–3 cycles of purification. CsPbBr3 NCs assume a nonluminescent state, whereas MAPbBr3 NCs quickly decomposed. The PL properties and stability of purified FAPbBr3 NCs were then investigated in films (Figure 3). A small, 5–10 nm shift in the PL peak is systematically seen upon preparation as films, compared to the solution spectra. The time-resolved (TR) PL traces from solutions of 12 nm NCs (Figure 3c) and from smaller NCs (8 nm, Figure S7) are monoexponential with lifetimes of 25 and 7 ns, respectively. Such a size effect can be attributed to the higher exciton binding energy in such small crystallites due to quantum confinement. The QYs for both NC sizes were >70%. Contrary to conventional quantum dots, such as CdSe and InP NCs, perovskite NCs feature unusual, defect-tolerant photophysics,13 i.e., surface dangling bonds and intrinsic point defects such as vacancies do not form a high density of midgap states, known to trap carriers and thereby quench PL. CdSe and InP NCs, being defect-intolerant, require epitaxial passivation layers to exhibit bright PL. TR-PL traces from films of 12 nm FAPbBr3 NCs show two characteristic lifetimes: one similar to the corresponding colloidal solution and a second, longer component (40 ns) that can be attributed to increased exciton delocalization. The longer-living component has not been observed in the closely related CsPbBr3 NC system.2 FAPbBr3 NC films that were dried at room temperature exhibited QYs up to 81%, whereas films dried at 50 °C for 24 h in air exhibited reduced QYs of 70%. The ability of FAPbBr3 NCs to retain bright PL also in the polymer-embedded form and under mild heating at 50–60 °C was then investigated. Such luminescent polymer films might eventually be used as backlight films in television displays.

NCs were mixed with poly(methyl methacrylate) (PMMA) in toluene, followed by drying at 50 °C for 4 h in air. These as-prepared films exhibited QYs of ~65%, without noticeable deterioration after 24 h. Higher temperature annealing (at 100°C, 4 h) still resulted in high QYs of ~50%. Identical experiments with CsPbBr3 NCs led to QYs not exceeding 10% (Figure S8). Long-term-stability of FAPbBr3 NC films requires additional investigations and further improvements are expected through various encapsulation strategies (core–shell morphologies, embedding into crystalline matrix, etc.).

High PL QYs and exciton delocalization may assist in achieving lasing from FAPbBr3 NC emitters.5a

Figure 4. Amplified spontaneous emission (ASE) from a film of ~12 nm FAPbBr3 NCs. Inset: threshold behavior for the intensity of the ASE band.
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