N-Methylformamide as a Source of Methylammonium Ions in the Synthesis of Lead Halide Perovskite Nanocrystals and Bulk Crystals

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Supporting Information

ABSTRACT: We report chemical routes for the synthesis of both nanocrystals and bulk crystals of methylammonium (MA) lead halide perovskites employing N-methylformamide (NMF) as a source of MA ions. Colloidal nanocrystals were prepared by a transamidation reaction between NMF and an alkyl amine (oleylamine). The nanocrystals showed photoluminescence quantum yields reaching 74% for MAPbBr₃ and 60% for MAPbI₃. Bulk crystals were grown at room temperature, with no need for an antisolvent, by the acid hydrolysis of NMF. Important advantages of using NMF instead of MA salts are that the syntheses involve fewer steps and less toxic and less expensive chemicals.

The rapid increase in the power conversion efficiencies of solution-processed hybrid lead trihalide perovskite solar cells has captured worldwide attention and has started a race on developing new synthesis approaches and studying the many fascinating properties of these materials. Besides solar cells, hybrid perovskites have demonstrated significant performance as active layers in several other optoelectronic devices, including photodetectors and light-emitting diodes. Another notable feature of hybrid perovskite-based devices is their facile solution processability. Hybrid perovskites can be fabricated as nanocrystals (NCs), thin films, or single crystals. Each of these forms has peculiar optical and/ or electrical properties. For instance, NCs of CH₃NH₃PbBr₃ (MAPbBr₃) have an absorption onset at 505 nm, while the thin films and single crystal counterparts have absorption onsets at 544 and 570 nm, respectively. Each of these forms has its own preferred fields of application: thin films are ideal for solar cell devices, while NCs are superior in display technology due to their higher photoluminescence quantum yield (PLQY). On the other hand, single crystals, besides having been employed in optoelectronic devices, represent the best platform to determine the actual properties of the material such as the carrier diffusion length and lifetime.

To date, the synthesis of MAPbX₃ (X = Cl⁻, Br⁻, or I⁻) perovskites has been carried out using methylammonium salts (MAX) as precursors for methylammonium (MA) ions. These salts are generally prepared by the dropwise addition of HX to an ethanolic solution of methylamine. After 2 h of stirring in an ice bath, MAX is then recrystallized and dried overnight. The in-house synthesis of MAX is a common step in most research groups as the commercially available MAX salts are costly. The second step involves mixing the dried MAX with the corresponding PbX₂ salt in an appropriate solvent. Dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF), γ-butyrolactone (GBL), are the apt solvents to fabricate bulk-scale Cl-, Br-, and I-based perovskites, respectively. This is attributed to the different solubilities of the precursors in these solvents. In the case of the best platform to determine the actual properties of the material such as the carrier diffusion length and lifetime.

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colloidal perovskite NCs, multiple synthetic methodologies, including ligand-assisted reprecipitation and hot injection techniques, have been developed for the synthesis. Unlike the all-inorganic CaPbX3 NC counterparts, which are mainly obtained in cubic shapes of around 7–8 nm in size, MAPbX3 NCs are synthesized in roughly spherical shapes with sizes around 3.3–6 nm. A recent hot injection synthesis by Vybornyi et al. could deliver cubic shapes for MAPbI3 NCs and nanoplatelets for MAPbBr3, but apparently could not be extended to MAPbCl3 NCs.

Herein, we report a general route involving fewer steps, less toxic chemicals, and reduced cost for the fabrication of MAPbX3 perovskites in both NCs and bulk forms, compared to the various previous approaches reported. Our method proceeds without first synthesizing and purifying MAX, as well as avoiding procurement of expensive MAX salts and eliminating the use of toxic DMF. We used instead N-methylformamide (NMF) as a source of MA through a transamidation reaction between NMF and oleylamine (OLA, Scheme 1), to synthesize colloidal MAPbX3 NCs with a record PLQY of 60% for the MAPbI3 NCs. Bulk crystals were grown from NMF and PbX2 in the presence of a hydrohalic acid (HX, aqueous solution) as a result of the acid-catalyzed hydrolysis of NMF (Scheme 1), as previously reported for DMF and other amides. Unlike other MAPbX3 crystallization techniques (see Table S1), our free-standing Cl-, Br-, and I-based bulk crystals (in addition to the mixed Cl/Br and mixed Br/I bulk crystals that we could prepare) grow at room temperature (RT) and without any antisolvent.

We start our discussion on the release of methylammonium or methylamine respectively from NMF by either transamidation or acid hydrolysis, as shown in Scheme 2. Figure 1a,b reports the nuclear magnetic resonance (NMR) analysis involving 1H NMR and 13C NMR combined with heteronuclear single quantum coherence (HSQC) on the transamidation reaction of NMF with OLA. It reveals that there is a partial transformation of the amine (OLA) into the amide (N-oleyl formamide) and, in parallel, a partial conversion of the starting amide (NMF) to the amine (methylamine). According to the 1H NMR spectrum recorded in DMSO-d6 after 10 min of mixing at 100 °C, two new signals at 3.05 ppm (a pseudo quartet, J = 6.70, 6.47 Hz) and a singlet at 2.25 ppm were observed. The intensities of the new signals became more pronounced if the reaction was run for longer times. The multiplicity-edited HSQC for the CH3 signal in position α to an N group returned cross peak 2 at 2.49 and 41.4 ppm for the amine (OLA), while cross peak 1 was shifted to 3.05 and 37.5 ppm for the amide, which is compatible with the transformation of the amine (OLA) into the amide. Opposite shifts from 2.6 and 24.6 ppm to 2.25 and 28.6 ppm for the CH signal are observed (cross peaks 4 and 5), indicating the formation of methylamine from NMF. Further support of the N-oleyl formamide formation was inferred from the heteronuclear multiplet-bond correlation spectroscopy (HMBC) inset in Figure 1b. A 1,3 interaction was observed between signal 1 and the 13C resonance at 161.2 ppm, which is typical of an amido CO group but is different from those of NMF (161.8 and 165.2 ppm).

Next, we investigated the in situ formation of methylammonium through NMF acid hydrolysis. Using deuterium chloride (DCl), 35 wt % in D2O, at a DCl/NMF volume ratio of 1:9, no hydrolysis took place after immediate mixing; the NMR spectrum was identical to that of NMF in D2O. However, if the mixture was left stirring for 24 h before analysis, two extra peaks were observed in the 1H NMR (Figure 1c). Those two extra peaks correspond to a CH3 bound to a protonated amine group (5) and a C–H of formic acid (6). Similarly, two extra peaks were observed in the 13C NMR, as shown in Figure 1d, corresponding to a C of a methyl bound to an amine group and to the CO of formic acid (its identity was further confirmed by spiking the sample with authentic formic acid, observing, in this way, an intensity increment of the signals). These data indicate partial hydrolysis of NMF and the possibility of in situ formation of methylammonium formate (MAF), which was previously reported to be used as an additive in the perovskite solution to promote a slower crystallization process, resulting in larger-grain perovskite thin films.

We then exploited the transamidation of NMF with OLA as a means of delivering MA ions in the synthesis of colloidal MAPbX3 NCs. We adapted the synthesis described by Huang et al. but used NMF instead of DMF and the MAX. In the present system, PbX2 and the capping ligands oleic acid (OA) and OLA were dissolved in NMF, forming a precursor solution that contained all of the reactants needed for the synthesis. After this solution was heated at 100 °C for 10 min, it was cooled at room temperature (RT) and then injected into a “bad solvent”, such as dichlorobenzene (DCB) or chloroform (CHCl3), heated at the desired temperature (from RT up to 120 °C), under vigorous stirring. Almost immediately after the injection, strong fluorescence from the flask indicated the formation of the MAPbX3 NCs. Preheating of the precursor solution at 100 °C, as well as the presence of OLA in it, was necessary for the synthesis. According to the NMR data discussed earlier, MA ions are produced in the precursor solution upon heating by a transamidation reaction between

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**Scheme 1. Sketch of the Two Different Routes, Both Employing NMF as a Source of MA Ions for the Synthesis of Either Perovskite NCs or Bulk Crystals**

**Scheme 2. Reaction Scheme for NMF Transamidation and Acid Hydrolysis with Numbering of the Highlighted Protons**

**Transamidation**

\[
\text{H} - \text{O} \quad \text{H}_2\text{N-}R \quad \text{NH}_2 \quad \text{H} - \text{O} \\
\downarrow \quad \text{10 min at 100 °C} \quad \text{10 min at 100 °C} \\
\text{H} - \text{NH}_2 \quad \text{H} - \text{NH}_2 \\
\]

**Hydrolysis**

\[
\text{H} - \text{NH} \quad \text{D}_2\text{O}/\text{DCI} \quad \text{D}_2\text{O}/\text{DCI} \quad \text{H} - \text{O} - \text{D} \\
\downarrow \quad \text{24 hrs at RT} \quad \text{24 hrs at RT} \\
\text{H} - \text{NH}_2 \quad \text{H} - \text{NH}_2 \\
\]

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NMF and OLA (in analogy with various types of transamidation reaction reported in the literature). X-ray diffraction (XRD) patterns of the various NC samples confirmed the cubic structure for both MAPbCl₃ and MAPbBr₃ NCs and the tetragonal phase for the MAPbI₃ NCs (Figure S1). This method enabled the synthesis of uniform, phase-pure colloidal NCs of Cl-, Br and I-based perovskites. Figure 2a−c reports transmission electron microscopy (TEM) images of representative samples having cubic shapes (see Scheme S1 and Table S2 for details on their syntheses). The resulting MAPbX₃ nanocubes had an average length of 21 ± 7 nm for MAPbCl₃ NCs, 25 ± 3 nm for MAPbBr₃ NCs and 17 ± 5 for I-NCs. The MAPbBr₃ and MAPbI₃ NCs remained well dispersed for weeks. The MAPbCl₃ NCs had a broader size distribution than the MAPbBr₃ and MAPbI₃ NCs, which resulted in tailing in the absorbance spectrum of the MAPbCl₃ sample and a partial sedimentation of NCs after a couple of days. The absorbance onsets and PL peak positions with full width at half-maxima of 0.116, 0.108, and 0.092 eV for the Cl-, Br and I-based perovskites, respectively, were in good agreement with previously reported data (Figure 2d). Remarkably, the MAPbBr₃ and the MAPbI₃ NCs had high PLQYs (74 and 60%, respectively). To the best of our knowledge, the PLQY measured for the MAPbI₃ NCs is the highest reported so far. Previous syntheses of MAPbI₃ NCs have reported typical PLQY values between 20 and 30%. The MAPbCl₃ NCs had instead low PLQYs (~3%). Similar trends in PLQYs of halide perovskite NCs (with the MAPbCl₃ NCs hitting the lowest values among the three halides) have also been reported for CsPbX₃ NCs.21,22 One important parameter of this approach is the injection temperature. For example, in the synthesis of MAPbBr₃ NCs, by adjusting the temperature of the bad solvent (in this case...
DCB was used), it was possible to synthesize blue-emitting spherical particles (at 60 °C; see Figure S2) or green-emitting cubic-shaped NCs (at 100 °C; see Figure 2b). The same reaction at higher temperature (130 °C) yielded sheets with broad lateral size distributions (Figure S3A). As shown in previous works, the growth of MAPbI3 NCs is faster than that of Br- or Cl-based perovskite NCs.24 The same trend was found here. For example, cubic-shaped MAPbCl3 could be grown only by heating the bad solvent at 120 °C (Figure 2c), while in the case of MAPbI3 NC, heating the bad solvent yielded bulk, nonemitting particles (Figure S4A). Even a RT synthesis (still using DCB as the bad solvent) led to a nonemitting sample formed by bulky nanowires (Figure S4B). Instead, strongly fluorescent cubic-shaped NCs could be grown using CHCl3 as a bad solvent (Figure 2a). The rapid cooling of the flask after the injection was another crucial step in order to avoid the growth of large and poorly emitting NCs. For instance, in the case of MAPbBr3 NCs, increasing the reaction time up to 10 s led to NCs with a lower PLQY (50%); see Figure S3B).

We then explored how the acid hydrolysis of NMF could act as a source of MA ions in the synthesis of bulk MAPbX3 crystals. Bulk crystals of different halide perovskites were successfully grown within 12–48 h at RT by a judicious choice of the Pb precursor concentration and the HX/NMF ratio, as shown in Scheme 1 and Table 1. Bulk MAPbBr3 crystals (4 × 4 × 2 mm) with a relatively smooth surface (Figure S5) were formed with a PbBr2 concentration range of 0.2–0.8 M and a HBr/NMF volume ratio of 1:5.7. Crystals grown from 1 M PbBr2 solution could reach 7 × 7 × 3 mm if kept in the solution for 4 weeks (Figure S5). Lower concentrations did not produce any crystals even if left for several days. The crystallization speed could be increased if the process was carried out at temperatures higher than RT or by using higher HBr concentrations. In these cases, however, several aggregated crystals were formed (Figure S6). It is worthwhile mentioning that bulk perovskites could also be grown using lead acetate (Pb(Ac)2) or lead thiocyanate instead of lead bromide (Figure S7). In the case of the MAPbCl3 crystals, single nucleation in the crystallization vial was possible by lowering the concentration to 0.2 M with a HCl/NMF ratio of 1:9. The final crystals were about 3 × 3 × 2 mm large but were not fully transparent. Smaller crystals (2 × 2 × 1 mm) with higher transparency could be formed at earlier stages of crystallization or by working at higher HCl content, but these conditions induced multiple nucleation events (Figure S8). On the other hand, the I-based perovskites could precipitate out of the HI/NMF solution mixture only if the NMF content was reduced below 20% of the total volume. In this process, NMF plays the dual role of solvent and the source of MAX. NMF, as a highly polar solvent, can bind strongly to the iodide precursors; hence, the MAPbI3 crystals are stable only at a lower NMF content. This appears to be in agreement with previous reports, according to which the less polar GBL, rather than the strongly polar DMF, is used for the crystallization of MAPbI3.10,11

The RT grown MAPbI3 crystals using low NMF content (HI/NMF 10:1) were small and formed aggregates in the crystallization vial (Figure S9). Aggregates made up of much larger MAPbI3 crystals could be grown using (Pb(Ac)2) instead of PbI2 (Figure S9). This aggregation problem could be overcome by two different routes: either by using a concentrated (1.3 M) PbI2 solution in a HI/NMF ratio of 16:1 (Figure S10) or by using stabilized HI (H3PO2-containing HI) (Figure S11). Crystals prepared using stabilized HI had to be heated at ~60 °C for 30 min, after being removed from the crystallization dish; otherwise, they turned yellow within a few seconds. On the other hand, after the heating process, they remained black for days. The free I2 or the I3− present in the unstabilized HI may be the reason for the aggregation as they may engage in halogen bonding with undercoordinated halide ions.38 As a result of this halogen bonding, a passivating layer could be formed on the surface of the MAPbI3 crystals grown from unstabilized HI (I3−-containing HI). Therefore, these MAPbI3 crystals did not require postheating treatment. Importantly, whether stabilized or unstabilized HI was used, the collected crystals had a smooth shiny surface.

According to the XRD patterns of ground crystals, their phases matched with those of the previously reported samples of the same materials, namely, the cubic phase for MAPbCl318 and MAPbBr310,11 and the tetragonal phase for MAPbI310,11 (Figure 3a). The XRD pattern of the Cl- and Br-based as-
when the PL was excited with one-photon laser excitation, which has a shallow penetration depth, it was blue-shifted. For example, the PL spectra from the bromide and iodide bulk crystals were peaked at 550 and 780 nm, respectively (Figure S13a,b). Both values are blue-shifted from the corresponding bulk values (580 nm for bromide crystal and 820 nm for the iodide crystal). In Figure 4, we show the time-resolved PL dynamics and spectra collected from bulk crystals of MAPbI₃ and MAPbBr₃. The excitation for both samples was tuned to 480 nm, and the measurements were performed in ambient conditions. In the case of the MAPbI₃ crystals, we observed an intensity-dependent dynamics, with a clear bimolecular recombination evident at high excitation densities. Similar dynamics have already been observed in other single crystals and are indicative of efficient radiative recombination after the saturation of carrier traps.

The excitation density at which the bimolecular recombination becomes strongly evident qualitatively represents the available trap density. Following the density dependence shown in Figure 4a, we conclude that the trap density in these crystals is lower or at around 10¹⁶ cm⁻³. It must be noted that this value is lower than what is typically observed in polycrystalline thin films. However, due to the limited penetration depth of the excitation, we were predominantly probing the dynamics at the crystals surface, which is inherently prone to a higher density of defects with respect to the bulk. In fact, when the sample was kept under vacuum, due to the absence of passivating oxygen, we observed slower trap-limited dynamics due to enhanced defect density (Figure S14a). In the case of MAPbBr₃, on the other hand, we observed intensity-independent dynamics at the probed excitation densities (Figure 4b), suggesting that we were well within the trap-limited regime with higher density of defects than MAPbI₃. Here again, we observed a quenching of the lifetimes when the sample was kept under vacuum due to the increase in the defect density (Figure S14b).

Very recently, MAPbI₃ crystals grown from an aqueous HI solution were reported to possess higher crystallinity and lower trap-state density compared to crystals grown from GBL solution. Additionally, in hybrid perovskite thin films, it has been previously reported that an optimal amount of water assists the perovskite crystallization and leads to a larger grain size. In our process, the water content was adjusted indirectly by proper choice of the HX/NMF ratio. Generally, water in the perovskite precursor solution may dissolve the organic cation but cannot dissolve the PbX₂ precursor, leading to a nonstoichiometric material. This is not the case in our crystals as the XRD patterns showed no extra peaks corresponding to any PbX₂ salts. Another possible effect of the water content in our procedure is in regulating the rate of NMF hydrolysis, which is the vital step for the controlled release of MA.

The present NMF-assisted procedure could also be used to synthesize mixed halide perovskite bulk crystals, as indicated from the XRD pattern shift and the color of the crystals (Figure S15). Mixed Cl/Br crystals were grown using PbBr₂ and HCl.

Figure 4. Time-resolved PL dynamics and spectra collected in ambient conditions from the single crystals of (a) MAPbI₃ and (b) MAPbBr₃. The excitation for both samples was tuned to 480 nm, and dynamics were taken at excitation densities in the range between 10¹⁴ and 10¹⁶ cm⁻³, as indicated in the figure legend.

Figure 5. (a) XRD pattern and (b) SEM image of a microcrystalline film of MAPbBr₃. (Inset) Picture of a 1.5 × 1.5 cm film.
while the mixed Br/I were formed using the same conditions for pure MAPbBr3 bulk crystals (1 M PbBr2 in HBr/NMF, 1:5.7), followed by the addition of 250 μL of HI to 1 mL of the bromide solution. The minor shift in the case of the mixed Br/I could be attributed to stronger complexation between Pb2+ and Br− compared to that between Pb2+ and I−.44 When using PbBr2 and HI, without any HBr added, pure MAPbI3 crystals were formed. While single crystals represent the ideal form to investigate the materials’ properties, their large thickness limits their use in high-performance device applications. To this end, as a proof of concept, we exploited such an NMF procedure to fabricate planar-integrated single-crystal (ISC) perovskites—microcrystalline films made of interconnected micron-sized crystals (Figure 5), similar to what was previously reported to fabricate one of the best-performing MAPbBr3-based photodetectors.7 By introducing some stirring force into the crystallization dish, microcrystalline films could be formed on both glass and ITO substrates.

In conclusion, we have developed a general and effective procedure for the synthesis of NCs and bulk crystals of MAPbX3. This procedure takes advantage of the in situ formation of MA via transamidation with alkyamine or acid-catalyzed hydrolysis of NMF, hence reducing the amount of work, chemical toxicity, and cost required to realize high-quality perovskites. Importantly, strongly fluorescent MAPbX3 NCs (with record PLQY for the MAPbI3 NCs of 60%) could be synthesized using NMF and OLA by a simple reprecipitation process, without the need for degassing any solvents. Moreover, only through this NMF hydrolysis strategy can bulk crystals be grown without heating and without any antisolvent. In principle, with the method described here, MA ions can be released “on-demand” during a process, for example, by increasing the acidity of the medium or by raising the local temperature, which might enable better control of the fabrication of this important class of materials. These possibilities are currently being studied in our groups.

■ ASSOCIATED CONTENT

# Supporting Information

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Materials, experimental and characterization details, SEM images, additional TEM images, and XRD patterns (PDF)

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Notes
The authors declare no competing financial interest.

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