Molecular Iodine for a General Synthesis of Binary and Ternary Inorganic and Hybrid Organic-inorganic Iodide Nanocrystals

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ABSTRACT: We report the synthesis of various binary and ternary inorganic and hybrid organic-inorganic iodide nanocrystals starting from molecular iodine (I₂). The procedure utilizes a reaction between I₂ and oleylamine that yields oleylammonium iodide – the iodide precursor for a subsequent preparation of nanocrystals. The syntheses are facile, carried out under air, in vials heated on a hotplate and deliver nanocrystals with narrow size distributions and, in the case of red and near infrared-emitting lead-based perovskites, with 70-80% photoluminescence quantum yields. The latter were used to fabricate red and infrared bright light-emitting diodes, with external quantum efficiencies (EQE) exceeding 3%.

Metal halide nanocrystals (NCs) have gained increasing attention in past years. Among these metal halide NCs, the halide perovskite (APbX₃ with A = Cs⁺, methyl ammonium (MA) or formamidinium (FA), B = Pb²⁺ or Sn²⁺ and X = Cl⁻, Br⁻ or I⁻) NCs are by far the most studied ones, due to their excellent optical properties and their relatively simple synthesis methods. The strong interest in these halide perovskite NCs has also motivated the development of synthesis approaches for other colloidal halide based NCs. This interest is mainly driven by the search for lead-free perovskite alternatives to the Pb-based ones for applications in photovoltaics and lighting. This has led for instance to reports on synthesis of ternary Cs₄SnI₉, Cs₄Bi₂X₉ and Cs₄Sb₂X₉ NCs, and quaternary Cs₂AgBiX₆ double perovskite NCs. Another group of interesting new metal halide NCs emerging from the perovskite NC research are the Cs₄PbX₆ NCs as well as simple cesium halide NCs.

The vast majority of colloidal metal halide NCs are nowadays prepared based on the colloidal synthesis scheme of CsPbX₃ NCs reported by Protesescu et al., were a Cs-oleate solution is quickly injected into a hot solution of the metal halide precursor (for example PbX₂ dissolved in octadecene (ODE), oleylamine (OLAM) and oleic acid (OA)). Although this method yields high quality perovskite NCs, it does not allow to control the Pb:halide molar ratio introduced in the synthesis and moreover it relies strongly on the solubility of the metal halide precursors in the ligand/solvent mixture. Also, this method cannot be generalized, as many metal halides (for example AgBr and PbCl₂) are difficult to dissolve in simple OA and OLAM mixtures and additional ligands (like trietyl phosphine oxide) are required. Other issues are related to the high costs and instability of certain metal halide salts, like for example most transition metal iodides. These precursors are often highly reactive, and not much work has been done towards controlling the precursor reactivity, as opposed to the extensive research devoted to identify suitable chemicals for the synthesis of the more traditional cadmium and lead chalcogenide NCs. Developing synthetic methods where elemental ratios, especially between cations and anions, can be tuned independently, is an important goal in the preparation of multinary materials, and is also relevant for metal halide perovskites. To this end, both Creutz et al. and Imran et al. recently reported a different method to prepare metal halide NCs, where a reactive halide precursors (either trimethylsilyl halide or benzoyl halide) is injected into a solution of metal acetate salts. Imran et al. for example demonstrated that this synthesis can be extended to various perovskite NCs by simply choosing the proper precursors and optimizing the reaction conditions. Although the use of trimethylsilyl halides or benzyl halides resulted in perovskite and double perovskite NCs with narrow size distributions, these chemicals are air sensitive, which prevents their use in the syntheses under ambient conditions (i.e. under air).

Here, we report a general synthesis route to binary and ternary inorganic and hybrid organic-inorganic iodide NCs based on the injection of an OLAM-I₂ solution in an ODE solution containing metal or organic oleates. By selecting the appropriate metal or organic salt precursor, and by optimizing the ODE concentration and reaction temperature, inorganic and hybrid organic-inorganic iodide NCs of various compositions were prepared. All syntheses were performed under air, on a hotplate with off-the-shelf chemicals, highlighting the ease of the process and potential for high throughput synthesis. The nearly monodisperse lead iodide perovskite NCs prepared by this method had photoluminescence quantum yields (PLQYs) close to 80% and good stability over at least several weeks.
in air. These NCs were implemented as active layers in red and infrared light-emitting diodes with external quantum efficiencies (EQE) exceeding 3%. Additionally, other NCs such as CsPbI₃ and CsI NCs, and also several materials which have not yet been reported in the form of colloidal NCs, such as AgI, RbI, Kl, FA,Br,Br, and RbAg,Br, could be synthesized.

\[ \text{a) } 4 \text{RNH}_2 + I_2 \xrightarrow{120 \degree C} 2 \text{RNH}_3^+ + \text{RNH-HNR} \]

**Figure 1.** Formation of the oleylammonium precursor. a) Proposed reaction of iodine and oleylamine, leading to oleylammonium iodide (see also reaction scheme SI1); b) Optical absorption spectra of the OLAM-I₂ mixture before and after heating to 120 °C, indiacting the appearance of I⁻ species after heating (absorption band at around 220 nm); c) Selected region of ¹H NMR spectra of the OLAM-I₂ before and after heating to 120 °C. Upon heating, OLAM is protonated. Full spectra and assignment of resonances are reported in Figure SI2.

The iodide precursor used in the synthesis of the various NCs reported here was prepared by heating solid grains of molecular I₂ in a mixture of ODE and OLAM. This led to the *in situ* formation of oleylammonium iodide (Figure 1a). Such oleylammonium iodide/oleylamine precursor solution remained stable and no precipitate was seen at room temperature, even when stored in air. The same type of solution has been previously used by us to convert CsPbBr₃ to CsPbI₃ by anion-exchange. The mechanism leading to alkylammonium iodide by reacting amines with iodine has been already hypothesized in the 70s; it was proposed that the reaction goes through an oleylamine-iodine charge transfer complex, followed by a proton-iodine exchange, resulting in alkylamidoamine, hydro iodic acid and triiodide species (Scheme SI1 of the Supporting Information, SI). Finally, the *in situ* formed HI reacts with the oleylamine, resulting in the alkylationammonium iodide. This last step coincides with the synthesis of alkylammonium halides by reaction of amines with hydrogen halide solutions. Although it is difficult to confirm the formation of the various intermediates (and actually beyond the scope of this work), the presence of oleylammonium iodide can be proved with both optical absorption and nuclear magnetic resonance (NMR) spectroscopy. When, in our experiments, I⁻ was dissolved in OLAM at room temperature, the solution turned quickly dark brown and featured three absorption bands peaked at 250 nm, 360 nm, and 280 nm, which are ascribed to the I⁻ charge transfer complexes and to HI⁻ (Figure 1b). When the solution was heated up 120 °C, it quickly turned light brown (Figure SI1). The appearance of I⁻ (hence of oleylammonium iodide) upon heating could be tracked by optical absorption spectroscopy, as shown in Figure 1b. Here, the lower energy absorptions bands disappeared and a new strong absorption appeared at around 220 nm, matching that of previous reports on I⁻. ¹H NMR spectra of the OLAM-I₂ mixture were recorded before and after heating, as reported in Figure 1c and SI2. Before heating, resonances of the CH₃ in position α to the nitrogen of OLAM remained unchanged, indicating that under these conditions the amine does not get protonated, but it is rather engaged in a charge transfer complex with I⁻. After the OLAM-I₂ solution was heated to 120 °C, the α-CH₃ peaks exhibited an increase in chemical shift of 0.22 ppm. The extent of the chemical shift is close to that of the α-CH₃ peaks of OLAM in a 1:1 mixture with oleic acid, as discussed in a previous work of us, and ascribed to the protonation of OLAM. ²²

**Figure 2.** Lead iodide perovskite NCs. a-b) TEM images of CsPbI₃ and FAPbI₃ NCs indicating narrow size distributions; c) XRD pattern of CsPbI₃ and FAPbI₃ NCs matching with that the cubic perovskite crystal structure; d) absorption and PL of CsPbI₃ and FAPbI₃ NCs. XRD reference pattern of CsPbI₃ corresponds to 98-018-1288.

To explore the versatility of the OLAM-I precursor, both inorganic (CsPbI₃) and hybrid organic-inorganic (FAPbI₃) perovskite NCs were synthesized, as reported in Figure 2 (see the SI for details on the synthesis). The bright red-emitting CsPbI₃ NCs were about 12 nm in size, with PL peak centered at 688 nm (1.80 eV) and full-width at half maximum (FWHM) of 33 nm (~86 meV). The bright near-infrared-emitting FAPbI₃ NCs, about 14 nm in size, had a PL spectrum centered at 762 nm (1.62 eV) and full-width at half maximum (FWHM) of 64 nm (~138 meV). The freshly made solutions of CsPbI₃ and FAPbI₃ NCs had high PL quantum yields (PLQY) of 79±4% (CsPbI₃ NCs, under 508 nm excitation) and 74±3% (FAPbI₃ NCs, under 600 nm excitation). Both the CsPbI₃ and FAPbI₃ NCs evidenced multieponential PL decays with similar 1/e lifetimes of ~40 ns under 508 nm excitation. Both the CsPbI₃ and FAPbI₃ NCs evidenced multieponential PL decays with similar 1/e lifetimes of ~40 ns under 508 nm pulsing excitation (Figure SI3). These red-emitting lead iodide perovskite NCs prepared from off-the-shelf chemicals under air on a hotplate had therefore optical properties on par with the ones synthesized under inert atmosphere with degassed precursors. In addition to the emissive iodide perovskite NCs, wide-gap zero-dimensional CsPbBr₃ NCs could also be synthesized, simply by increasing the Cs:Pb ratio, as shown in Figure SI4. ¹⁰, ²⁴
We have exploited the excellent optical properties of the iodide perovskite NCs prepared with our simple approach to fabricate deep-red and infrared light-emitting diodes (LEDs). To remove excess ligands and ODE from the solution, a procedure often limiting the use of NCs in devices, a simple "rinsing" procedure was used (see experimental details in SI and scheme SI2). Here, after the NCs were separated from the growth solution through centrifugation, the vial was slowly (without shaking) filled with toluene, allowing for any residual organics attached to the vial to dissolve. The toluene was then removed, and the NCs were fully redispersed in toluene. The NCs samples to be used for LED fabrication were stored at high concentrations (6 times higher compared to normal storage). Under these conditions the NC were stable, as no significant loss of PL was seen after the samples were exposed to air for 2 weeks. The NC LEDs were prepared by spin-coating poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) on pre-patterned ITO/Glass coated glass substrates, followed by a layer of spin-coated NCs. The devices were finalized by evaporation of 2,4,6-Tris[3-(diphenylphosphinyl)phenyl]-1,3,5-triazine (PO-T2T) as hole blocking layer and Ca/Ag bi-layer metal contact (see SI for more details on device fabrication and Figure 3a for a schematic representation of the device stack and approximate energy levels). To prepare the mixed (Cs:FA)PbI3 NC LEDs, which are reported among the highest EQE among red/NIR NC LEDs, the CsPbI3 and FAPbI3 NCs solutions were simply mixed prior to devices fabrication. Due to interparticle cation exchange, the mixed solution exhibited a single PL peak and absorption centered between 688 nm and 762 nm, indicating a homogeneous (Cs:FA)PbI3 composition.

The electroluminescence spectra for all three devices (Figure 3b) evidenced single-peak emission at 688 nm (CsPbI3), 728 nm (mixed Cs/FAPbI3), and 739 nm (FAPbI3). This corresponds to a deep-red emission for the inorganic NCs with CIE coordinates (0.6489, 0.2856), thus promising for wide-gamut displays and lighting and near-infrared emission for the FAPbI3 and mixed-cation FA/CsPbI3 NCs. Figure 3c reports the current-voltage-radiant flux curves of the three devices. The highest radiant flux was obtained for purely inorganic CsPbI3 NCs, exceeding \(10^6 \, \text{µW/m}^2\) at 8 V. This corresponds to XXX cd/m² (compare the value in cd/m² with literature). However, the most efficient devices were obtained with mixed Cs/FAPbI3, with external quantum efficiency (EQE) exceeding 2% in the whole range from 2.5 V to 7 V and an a maximum EQE over 3% around 4.3 V. These results are on par with record EQEs recently reported with NCs of similar chemical composition. Contrary to the other two devices, the one based on pure FAPbI3 evidenced a strong degradation of the radiance above 4V (Figure 3c) which ultimately led to lower EQE (Figure 3d). Interestingly, the incorporation of the inorganic cation Cs⁺ in the mixed NCs resulted in an increase of over one order of magnitude in EQE (Figure 3d) while maintaining an emission maximum close to that of pure FAPbI3 (Figure 3b).

The present synthesis approach could be easily extended to other iodide-based NCs in addition to the lead halide perovskites discussed above. As shown in Figures 4 and SI5, the injection of the iodine precursor in an ODE solution containing an alkali metal-oleate lead to the nucleation and growth of alkali iodide NCs with a narrow size distribution. The KI and RbI NCs crystallized in a simple cubic (Pm3m) crystal structure with cubic habit, whereas the CsI NCs crystalized into a face centered cubic (Fm3m) crystal structure, with cubo-octahedral habit. Similar to reports of CsI NCs, all the alkali metal NCs had an absorption band at around 220-230 nm, as shown Figure SI6. It is interesting to note the absorption band of these NCs is similar that of oleylammonium iodide (Figure SI7). These types of NCs should be interesting for use in scintillators, a common application for bulk CsI.
reference patterns of KI, Rb and CsI correspond to 96-900-8655, 96-900-8711 and 96-900-8791 respectively.

The ability to introduce iodine independent from the metal precursors in the reaction flask allowed us to extend the OLAM-I method to the synthesis of lead-free ternary bismuth iodide NCs. As shown in Figure 5a-b, both Cs$_3$Bi$_2$I$_9$ and FA$_3$Bi$_2$I$_9$ NCs could be synthesized. Whereas Cs$_3$Bi$_2$I$_9$ and MA$_3$Bi$_2$I$_9$ have been extensively investigated, mainly with the aim to replace lead based perovskites in photovoltaic devices, its organic formamidinium counterpart, FA$_3$Bi$_2$I$_9$, was only very recently reported as a bulk material. Both Cs$_3$Bi$_2$I$_9$ and FA$_3$Bi$_2$I$_9$ NCs crystallized in the Cs$_3$CrCl$_9$ crystal structure (Figure 5c), where isolated [Bi$_2$I$_9$]$^{3-}$ clusters made of two face-sharing octahedra are surrounded by ether Cs$^+$ or FA cations. Here, FA$_3$Bi$_2$I$_9$ is characterized by a slightly larger unit cell than Cs$_3$Bi$_2$I$_9$, due to the increased ionic radius of FA compared to that of Cs$^+$. Similar to previous reports, the Cs$_3$Bi$_2$I$_9$ and FA$_3$Bi$_2$I$_9$ NCs had a strong excitonic abortion peak around 500 nm (Figure 5d), originating from the absorption of the single [Bi$_2$I$_9$]$^{3-}$ clusters, which is almost identical for Cs$_3$Bi$_2$I$_9$ and FA$_3$Bi$_2$I$_9$, as the monovalent cation has very little influence on the optical transitions within the [Bi$_2$I$_9$]$^{3-}$ clusters.

Finally, the OLAM-I approach was extended to the synthesis of binary and ternary silver iodide based NCs. As shown in Figure S1b, both Ag$_3$I and RbAg$_4$I$_5$ NCs could be synthesized. RbAg$_4$I$_5$ is a superionic conductor which is characterized by a very high Ag$^+$ conductivity, even at low temperatures and is thus used as a solid electrolyte. This makes RbAg$_4$I$_5$, a promising material for all-solid-state super capacitors. The crystal structure of the RbAg$_4$I$_5$ NCs matches with that of previously reported RbAg$_4$I$_5$.

Overall, we have presented a fast and tunable synthesis method for a wide variety of metal iodide NCs. This protocol gives access to high quality lead halide perovskite NCs with PLQYs above 70%, but can also be used to screen new metal iodide based NCs, like the here reported KI, RbI, FA$_3$Bi$_2$I$_9$ and RbAg$_4$I$_5$ NCs. The use of a simple hot plate, in air, based method with a room temperature and air stable iodide precursor should enable its exploitation in the high-throughput synthesis of NCs, using for instance synthesis robots, or droplet-based microfluidic reactors. The high external quantum yield and narrow emission spectra obtained from LEDs incorporating the perovskite NCs confirms their high optical and electronic quality. Additionally, we demonstrate that the use of mixed NCs significantly improves the LED performance.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website at DOI: xxxxx.

 Experimental details of optical absorption, PL spectra, PLQY, PL lifetime measurements, PL decay curves

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