Green Emitting Lead-Free Cs_4SnBr_6 0D Perovskite Nanocrystals with Improved Air Stability

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ABSTRACT

It is reported the synthesis and characterization of nanocrystals of a novel fully inorganic lead-free 0D perovskite, namely Cs_4SnBr_6. Samples are made of crystal with average size around 20 nm with green emission centered around 530 nm. Interestingly, both colloidal suspensions and thin films show and enhanced air-stability with respect to any other previous tin-based nanocrystalline system, with emission persisting for tents of our under laboratory air.

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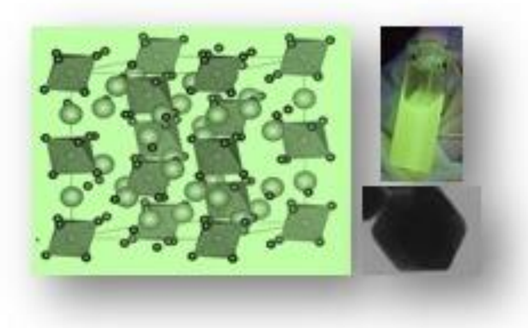

All-inorganic perovskite nanocrystals (NCs) represent a hot topic of current extensive investigation for their highly versatile optoelectronic properties such as, among others, very high photoluminescence (PL) quantum yields, tunable PL across the entire visible spectra range, and narrow full width at half-maximum of emission.[1-8] A very rich literature about this class of materials has been published following the key paper of Protesescu *et al*. reporting the synthesis of $CsPbX_3$ NCs by means of a standard hot-injection method.[9] More recently, strong attention has been also devoted to the preparation of lower-dimensional perovskite-related NCs, where the connectivity of the metal-halide octahedra can give origin to different dimensionality such as 2D, 1D and 0D phases.[2] Of particular actual interest, 0D perovskites derived from the well-known $CsPbBr_3$ NCs, *i.e.* Cs_4PbBr_6, has been subject of intense investigation.[10-18] Cs_4PbBr_6 is a green emitting compound with also a possible non-emitting phase obtained under certain synthetic conditions, with a debated origin of the peculiar PL properties, being possibly due to intrinsic lead ion emission, intrinsic defects within the wide bandgap of Cs_4PbBr_6 or to the presence of $CsPbBr_3$ nanocrystals.[18-19] By means of microemulsion method, the quantum yield (QY) of Cs_4PbBr_6 NCs has been found to be around 65% (in the colloidal form), with a small reduction of such value when transferred to thin films.[13] The peculiar crystal structure of 0D materials, where the octahedra are completely isolated by cation bridges and charge carriers are localized within the metal halide component, is a perfect test-bed sample to monitor the structural evolution of nanocrystalline systems from the 3D network to 0D molecular-like systems. Such peculiar arrangement, for example, allowed one to highlight an impressive tuning of Cs_4PbBr_6 NCs emission properties by pressure application.[20]

Despite the huge interest in all-inorganic perovskite NCs, the toxicity of lead is a major limitation, calling for a deep research into alternative lead-free materials.[21] As for the bulk perovskites, tin (Sn) is a possible replacement to Pb, and few examples of Sn-based NCs have been reported to date.[8,22-24] In particular, except for the “vacancy ordered double perovskite” Cs_2SnI_6, Sn-replacement has been used so far in 3D perovskites.[22-24] Sn-based halide perovskite

NCs tend to be highly unstable, with oxidation of Sn(II) to Sn(IV) occurring in just 5 minutes once the nanocrystals are exposed to ambient air.[24]

In order to fill a gap in the current literature we explored and developed the synthesis and properties of Sn-based 0D perovskite NCs, in particular the Sn-analogue of the most investigated Pb-based 0D compound, *i.e.*, Cs_4SnBr_6. To the best of our knowledge, there are not reports on the successful synthesis of tin-containing zero-dimensional perovskite NCs, while very recent papers reported the preparation and characterization of bulk materials.[25,26] In ref. 25, bulk Cs_4SnBr_6 was synthesized from melt-cooling, proving single-crystalline samples with broad-band PL centered at 540 nm with a QY of about 15%.[25] Moreover, in view of the peculiar crystal structure of 0D perovskites, being characterized by isolated octahedra, it is of interest to verify the relative stability to ambient conditions of these Sn-containing nanomaterials. As a matter of fact, in the present paper we could show a superior stability under air of Cs_4SnBr_6 nanocrystals for more than 48 hours, to be compared to few minutes of the analogue $CsSnBr_3$ 3D perovskite nanocrystals.[8]

Samples of colloidal nanocrystalline Cs_4SnBr_6 have been prepared with a classical hot-injection method (more details in the SI).

A sketch of the trigonal crystal structure (space group R-3c) of Cs_4SnBr_6 is reported in Figure 1a, showing the arrangement of isolated $[SnBr_6]^{4-}$ octahedra. Figure 1b reports a photo of the prepared NCs under ambient light and under UV-lamp, with a clear green emission visible in the samples under UV irradiation.

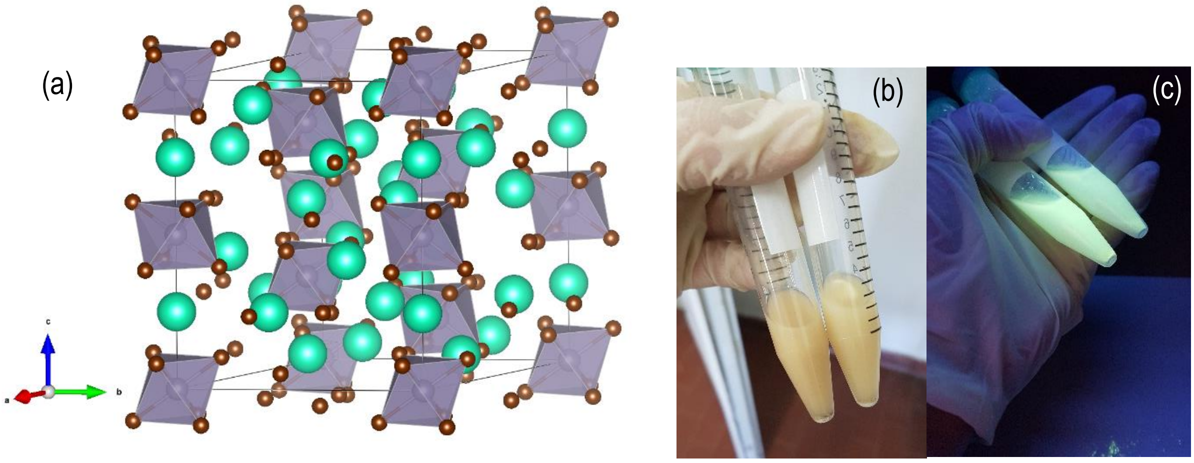

Figure 1. (a) Sketch of the Cs_4SnBr_6 crystal structure showing the isolated $[SnBr_6]^{4-}$ octahedra (in violet) and the Cs^+ ions (in green); (b) photo of the samples under ambient illumination and (c) under UV-light.

The x-ray diffraction (XRD) pattern of the prepared nanocrystals is reported in Figure 2a together with the reference pattern of the calculated crystal structure of Cs_4SnBr_6 (vertical red bars). As can be appreciated, the sample is single-phase with a very good agreement with the trigonal expected structure and without any appreciable preferential orientation of the sample. Lattice parameters obtained from the experimental pattern are a=b=13.683(3) Å and c=17.276(4) Å, which are in agreement with the single-crystal data reported by Benin *et al*.[25] The size of the prepared NCs has been determined by Transmission Electron Microscopy (TEM) and some representative images are reported in Figure 2b-d. The TEM images show a good homogeneity of the size distribution, as also inferred by the relative histogram in Figure 2e suggesting an average size around 18-22 nm. The peculiar hexagonal shape of the NCs can be seen in the enlargement of Figure 2d, and is analogous to the shape observed in Cs_4PbBr_6 for similar nanoparticle size.[13]

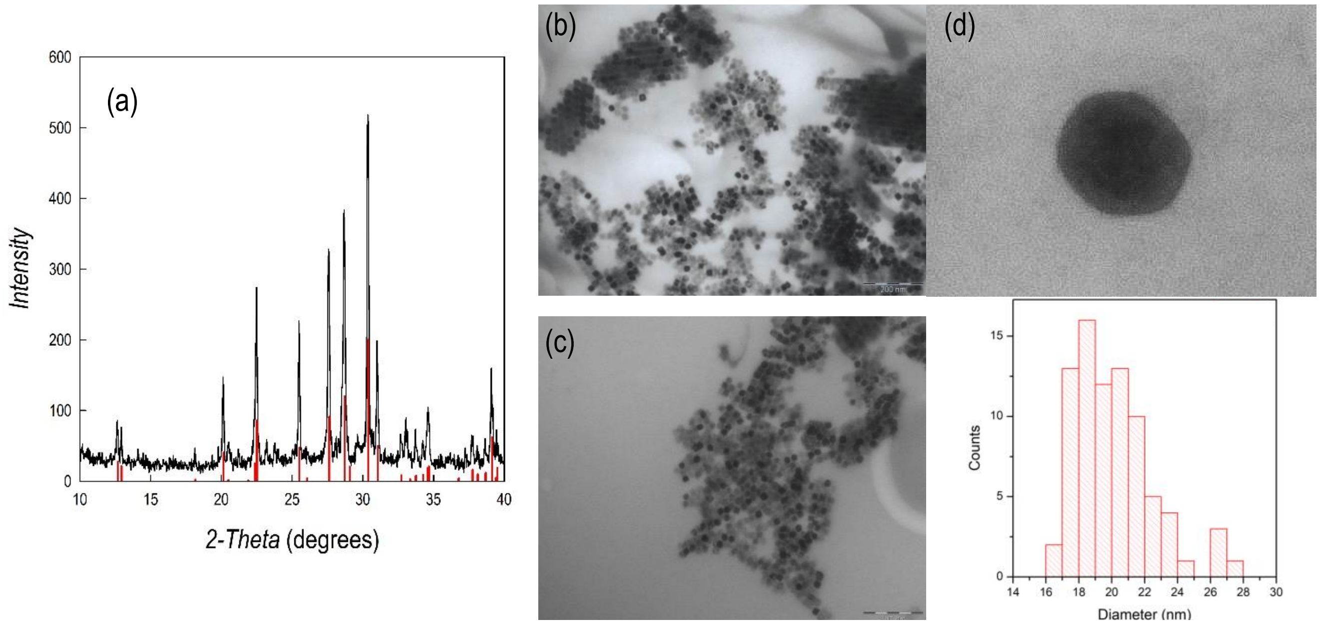

Figure 2. (a) X-ray diffraction of Cs_4SnBr_6 NCs (black line) superimposed to the calculated pattern taken from ref. 25 (vertical red bars); (b), (c) and (d) TEM images of Cs_4SnBr_6 crystals; (e) Size distribution histogram of Cs_4SnBr_6 NCs.

The optical properties of the prepared NCs have been studied by means of steady state and time-resolved PL spectroscopy, both on the colloids suspension and on thin films formed starting from the NCs suspensions. Figure 3a shows the PL for NCs and an exemplary thin film of about 100 nm of thickness. Both PL of Cs_4SnBr_6 NCs and film show a broad emission peaking at about 530 nm for both samples. This emission reasonably matches the PL maximum found at about 540 nm for the bulk samples of Cs_4SnBr_6.[25,26] QY determined on the NCs provided a value around 0.8%, which is lower with respect to Cs_4PbBr_6 NCs, but higher than other Sn-containing nanocrystals, which usually show quantum yields around 0.1-0.2%.[23-25] We also highlight that the present results suggest that the green emission is intrinsic to Cs_4SnBr_6 sample, since the correspondent 3D perovskite NCs, namely $CsSnBr_3$, emit at about 650 nm, and therefore the presence of this phase, at the interface with the 0D material, as a possible origin of emission, can be ruled out.[24] We mention this aspect since the emission from Cs_4PbBr_6 NCs is still strongly debated as possibly due to inclusions of $CsPbBr_3$ material, having an emission in the same range of the 0D perovskite.[27] Also very recently, this aspect has been further investigated in detail by Ray and co-workers, thus suggesting, with the present data, a way to further shed light on the emission properties of the lead-analogue of Cs_4SnBr_6.[27]

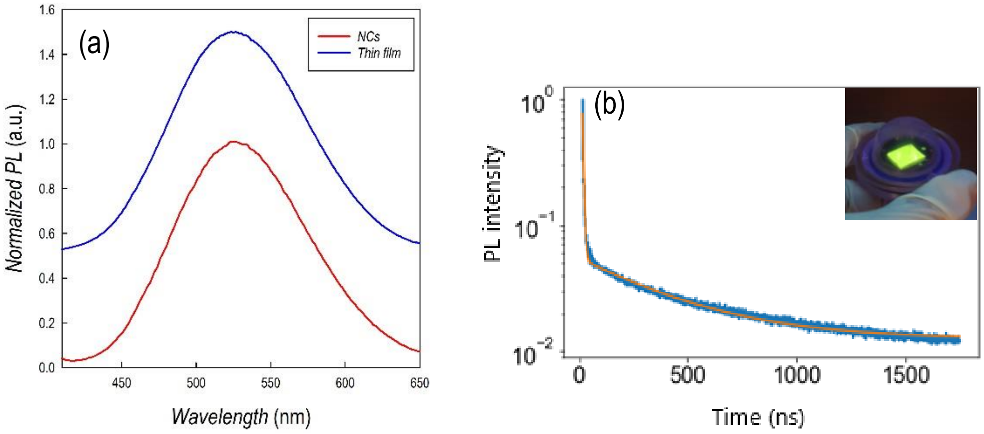

Figure 3. (a) PL spectra of Cs_4SnBr_6 NCs (red line) and thin film (blue line); (b) TRPL of Cs_4SnBr_6 thin films.

Steady state PL experiments have been conducted encapsulating the sample with a thin glass cover slide, upon exciting at XX and revealing the emitted light at XX. By looking at Figure 2a it is possible to note that there are not significant differences both in PL emission, centered at about 530 nm, and shape when moving from NCs to films, and the general features of the spectra reported also agree with those shown by bulk Cs_4SnBr_6.[25] On the other hand, the NCs of the 0D lead-containing Cs_4PbBr_6, for a similar size, show an emission at about 515 nm, with the red-shift possibly ascribable to the Sn replacement for Pb.[13] TRPL has been carried out on Cs_4SnBr_6 thin films and is reported in Figure 3b. Time resolved PL experiments have been conducted upon exciting the sample at XX and monitoring the emission at XX. The emission at the peak wavelength shows an initial fast decay (XX in amplitude, with a time constant t1=XX) and a second minor phase (amplitude XX) with long living tail extending in the μs window. The fast decay can be assigned either to rapid exciton or charge recombination or to fast charge trapping while the long living decay to a slower trap-mediated deactivation (IS THIS

IN AGREEMENT WITH USUALASSIGNEMENT?). Notably, the excitation light used is XX, which ensure a very low excitation density (from the Optical density we can estimate the number of photoexcitedcarriers/cm3or per dot) of the nanocrystals, enabling us to safely disregard any possible high order effects. Absorption measurements showed a long-tail without peak features in the range from 365 nm to 600 nm as also reported for Cs_4PbBr_6 nanocrystals and often observed in Sn-based nanosystems (reported in the SI).[13,24]

As mentioned above, one of the most significant issue related to Sn-containing perovskite NCs is their extremely poort stability under ambient air. In the present case we explored the stability of Cs_4SnBr_6 thin films by exposing them to laboratory air (40% relative humidity, 22°C) for several days and looking at their emission under an UV lamp. Figure 4 shows three photos of Cs_4SnBr_6 films: (a) is a film kept in a vial closed under argon, (c) is a film exposed for 4.5 days at ambient air, and (c) is a film at day 5 day of air-exposure.

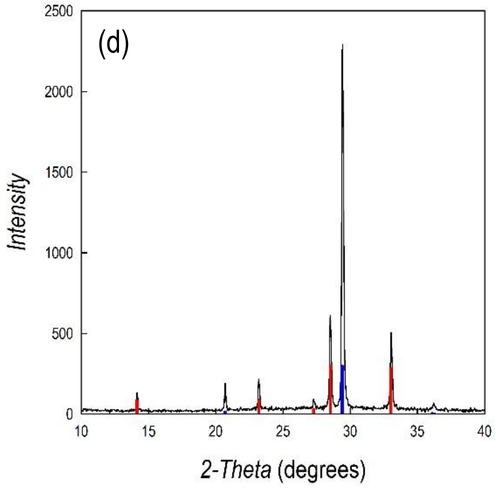

Figure 4. (a) Phot of a Cs_4SnBr_6 film kept in a vial filled with argon; (b) same film after 4.5 days of exposure to ambient air; (c) same film at day 5 after decomposition; (d) XRD pattern of the decomposed film.

Quite surprisingly, the Cs_4SnBr_6 film was still highly emissive after about 4.5 days under ambient air, which is a record stability for Sn(II) containing perovskite NCs. It is worth recalling that in all the previously synthesized Sn-containing NCs (3D perovskites), emission is quenched due to tin oxidation after few minutes under air exposure.[24] When emission is not seen any more in the present sample (at day 5), the film appears as reported in Figure 4c, and the corresponding XRD pattern, reported in Figure 4d, shows the presence of Cs_2SnBr_6, the vacancy ordered perovskite derivative containing Sn(VI), and CsBr. We also highlight that a film kept under argon into a vial is actually still emitting after more than 2 months of storage (see the Supporting Information) which compares to an average stability of Sn-containing NCs, under the same conditions, of about 2 weeks.[24]

Conclusions

In this paper we reported the first successful synthesis of 0D fully inorganic perovskite Cs_4SnBr_6 nanocrystals showing emission in the green region of the visible spectrum with a QY higher than corresponding tin-based 3D perovskites.[24] Crystal structure is similar to that of the Pb-based analogue, *i.e.* Cs_4SPbBr_6, while a small red-shift is shown in the PL emission peak when replacing tin for lead. Interestingly, the present nanocrystal always showed emission in all the synthetic routes and replica carried out, differently from Cs_4PbBr_6, and the present results can also rule out the possible presence of the corresponding 3D perovskite, namely $CsSnBr_3$ as the emitting phase included in the matrix having this last a red-emission.[24] More importantly, the present tin-based 0D nanocrystal showed impressive stability under humid air with a quenching of emission occurring after tents of our, with respect to the few minutes reported for $CsSnX_3$ nanocrystals. The present results pave the way for further optimization and tuning of 0D lead-free all inorganic nanocrystals showing superior air stability and further experimental and computational work is also planned to understand the microscopic origin of such improvement.

Supporting Information

Supporting Information Available

Acknowledgement

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