

## COMMUNICATION

Highly luminescent perovskite-aluminum oxide  
composites

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**In this communication we report on the preparation of  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  perovskite/ $\text{Al}_2\text{O}_3$  nanoparticle composites in a thin film configuration and demonstrate their high photoluminescence quantum yield. The composite material is solution-processed at low temperature, using stable alumina nanoparticles dispersions. There is a large influence of the alumina nanoparticles concentration on the perovskite morphology and on its photoluminescence.**

Recently, organic inorganic (hybrid) metal halide perovskites became the focus of renewed interest thanks to their remarkable performances in photovoltaics, as increasing power conversion efficiencies, now exceeding 20%, are being reported.<sup>1-6</sup> The most studied compounds in photovoltaics is the methylammonium lead iodide  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite, due to its strong bandgap absorption at about 1.6 eV. One of the interesting features of this class of semiconductors is that their optical properties can be modulated by simple substitution of their constituents.<sup>7</sup> The correspondent bromide compound  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  has a bandgap of about 2.3 eV, making it a good candidate for visible lasing and light-emission applications.<sup>8, 9</sup> For both applications, the active material should show high photoluminescence quantum yield (PLQY), in order to efficiently convert the generated (either electrically or optically) charges into photons. Unfortunately, the photoluminescence (PL) of hybrid perovskites depends on the excitation intensity, being high at very high excitation intensity while very low when the excitation intensity decreases.<sup>10</sup> In electroluminescence, this means that high current densities are needed in order to produce significant light emission, which leads to a low power conversion efficiency of the devices.<sup>8, 11</sup> A promising approach to reduce the non-radiative recombination in hybrid perovskites is the synthesis of nanoparticles. This had led to materials that show substantially enhanced photoluminescence, reaching PLQY exceeding 90%.<sup>12-15</sup> The nanoparticle preparation, however, relies on complex chemical synthesis which might

undermine the scalability of this approach. Moreover, the PLQY tends to substantially reduce when nanocrystals are processed as thin films, due to spontaneous aggregation of the perovskite.<sup>16</sup> It has also been shown how enhanced photoluminescence can be obtained by impregnation of a pre-formed mesoporous inorganic matrix (such as alumina) with the perovskite precursor solution, albeit a quantitative estimation of the PLQY has not been reported.<sup>17, 18</sup> From a film forming/processing perspective, a more appealing approach is the deposition of composites films from blends of polymer or low molecular weight organic semiconductors, resulting in the formation of nano-/micro- domains of the hybrid perovskites.<sup>19, 20</sup> Here we present a hybrid approach for the preparation of high PLQY perovskite-based materials, which consists in the processing of blends of the perovskite precursor with stable alumina nanoparticles (NPs) suspensions. Thin films were deposited at low temperature from solution, and PLQY up to 39% in the solid state were obtained. We show that the self-assembly of the alumina NPs constrains the growth of the perovskite to the nanoscale, resulting in the spontaneous formation of isotropic  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  nanocrystals.

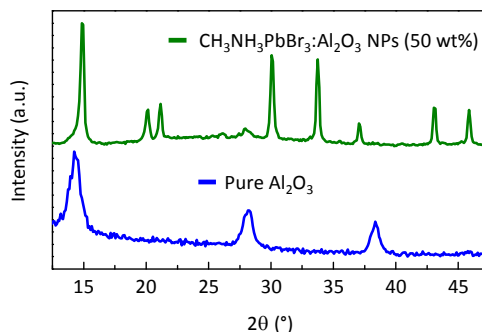


Fig. 1 GIXRD spectra of a mixed  $\text{CH}_3\text{NH}_3\text{PbBr}_3/\text{Al}_2\text{O}_3$  thin film compared to the reference obtained from a pure  $\text{Al}_2\text{O}_3$  NPS layer.

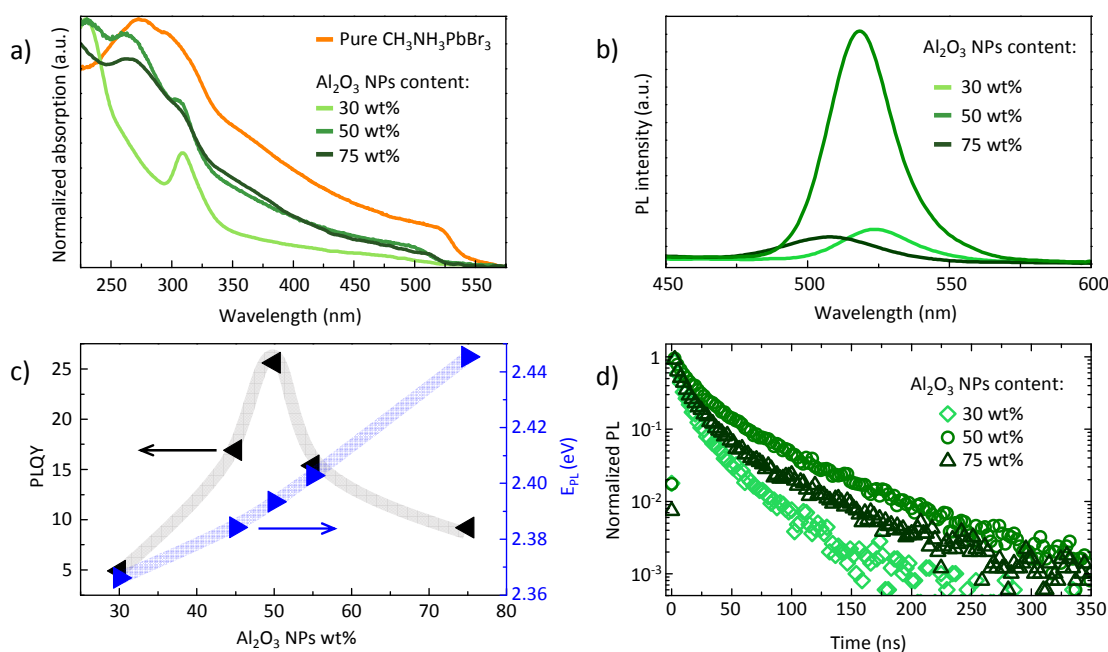


Fig. 2 Photophysical characterization of the composite  $\text{CH}_3\text{NH}_3\text{PbBr}_3/\text{Al}_2\text{O}_3$  NPs thin films for increasing NPs concentration. (a) Normalized UV-Vis spectra of the thin films, with the pure perovskite absorption reported as a reference, and (b) correspondent photoluminescence spectra recorded by exciting at 380 nm. (c) Trend of the PLQY (black, left) and of the energy of the PL emission peak (blue, right) vs.  $\text{Al}_2\text{O}_3$  NPs loading. The broad lines in (c) are drawn as guide to the eye. (d) Time-resolved PL measurements taken at the peak emission wavelength of each sample, with a pump wavelength of 380 nm.

The perovskite precursor solution was prepared by mixing  $\text{PbBr}_2$  and  $\text{CH}_3\text{NH}_3\text{Br}$  in DMF in a 1:3 molar ratio, respectively. Subsequently, an aqueous dispersion of  $\text{Al}_2\text{O}_3$  NPs with an average size of 10 nm, was added to the perovskite precursor. Different amounts of the  $\text{Al}_2\text{O}_3$  NPs to evaluate the effect of the perovskite/NPs ratio on the optical properties of the composite. Thin films of the composite materials were obtained by spin-coating the solution on glass or quartz substrates in air, followed by annealing on a hot plate at 90 °C for 1 hour. Processing of the composite films in air was possible due to their good stability to moisture. The origin of the relative moisture-insensitivity of the  $\text{CH}_3\text{NH}_3\text{PbBr}_3/\text{Al}_2\text{O}_3$  NP systems is not completely understood. In these films, however, most of the perovskite is surrounded by aluminum oxide, which is known to retard the degradation of hybrid perovskites.<sup>21</sup> On the other hand, pure  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  perovskite films were deposited and annealed in a nitrogen-filled glovebox, due to the limited stability of the compound in air.

The formation of crystalline perovskite was confirmed by grazing incidence X-ray diffraction (GIXRD) of the obtained thin films. In Fig. 1, the diffraction spectra of a composite film containing 50 wt% of alumina NPs is depicted. The spectra showed the diffraction pattern expected for  $\text{CH}_3\text{NH}_3\text{PbBr}_3$ , confirming the formation of the perovskite in the presence of a high concentration of alumina NPs.<sup>22</sup> The peak at 20.1° indicates that a small amount of the ammonium salt is still present in the composite film (See Fig. S1 in the supplementary information for the reference diffractogram of the pure  $\text{CH}_3\text{NH}_3\text{Br}$  and  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  compounds).

In Fig. 2a, the UV-Vis absorption spectra for a series of thin films with increasing  $\text{Al}_2\text{O}_3$  NPs content is depicted. The pure perovskite absorption spectra is shown as a reference. We observed that samples with low NPs content (30 wt%) are not fully converted to the perovskite structure with this annealing time and temperature, as testified by the spectral feature at ~310 nm which corresponds to lead bromide complexes.<sup>23</sup> By increasing the alumina NPs content,

the peak at 310 nm fades while the absorption onset at ~525 nm, corresponding to the band-to-band transition of the perovskite, appears. These observations suggest that the presence of alumina NPs favors the perovskite formation. A similar enhanced crystallization has been observed for  $\text{CH}_3\text{NH}_3\text{PbI}_3$  in mesoporous scaffolds.<sup>2</sup> Interestingly, perovskite/ $\text{Al}_2\text{O}_3$  NPs films with high NPs content (75 wt%) spontaneously form the crystalline perovskite phase even at room temperature (Fig. S2, supplementary information).

The photoluminescence characteristics of the  $\text{Al}_2\text{O}_3$  NPs thin films were studied using a Xe lamp coupled to a monochromator as the excitation source and a spectrometer coupled to an integrated sphere (Hamamatsu C9920-02 with a Hamamatsu PMA-11 optical detector) in order to quantitatively determine the PLQY. For the pure perovskite film and for films with a low NPs content (<30 wt%), only weak photoluminescence could be observed, with PLQY values within the measurement error of the setup (<2%). This is partially due to the low excitation intensity used in the experiments (< 0.4  $\text{mW}/\text{cm}^2$ ). On the other hand, with increasing NPs loading, the typical green emission of the  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  perovskite started to rise (Fig. 2b). A strong dependence of the PLQY on the  $\text{Al}_2\text{O}_3$  content is apparent which reaches a maximum of 26 % for a NPs concentration of 50 wt%. (Fig. 2c). This PLQY is slightly higher than what was reported for thin films of colloidal  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  nanocrystals.<sup>12</sup> This is particularly striking when taking into account the simple material preparation and its processing in air from water-based dispersions. By increasing the annealing time at 90 °C to 3 hours, the PLQY of the  $\text{CH}_3\text{NH}_3\text{PbBr}_3/\text{Al}_2\text{O}_3$  NPs (50 wt%) composite thin films is increased to 39 %. Together with the increase in the PLQY with increasing  $\text{Al}_2\text{O}_3$  NPs content a slight but continuous blue-shift of the emission energy occurs (Fig. 2d). This shift in emission wavelength was also observed in nano-sized  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  perovskite blended with organic semiconductors,<sup>19</sup> which was ascribed to quantum confinement effects. From GIXRD

line broadening, a crystallite size of about 20 nm for the films containing 30 wt%  $\text{Al}_2\text{O}_3$  NPs was derived. For such  $\text{Al}_2\text{O}_3$  NP concentration, the photoluminescence maxima was 2.37 eV, which agrees well with what was reported for similar size perovskites.<sup>19</sup> Even considering the rough estimation of the size by GIXRD, here we tend to exclude quantum confinement effects, since the predicted Bohr radius for  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  (2.2 nm) is significantly smaller than the particle dimensions obtained in the  $\text{Al}_2\text{O}_3$  NPs-perovskite composite films.<sup>24</sup> Recently, D'Innocenzo *et al.* observed a similar (in magnitude) blue-shift of the photoluminescence peak when decreasing the crystallite size of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  thin films.<sup>25</sup> They associated the measured shift with a distortion of the I-Pb-I bond, which has been theoretically predicted and also experimentally observed by Raman spectroscopy.<sup>26, 27</sup> Since such distortion would be especially significant in perovskites grown into a mesoporous scaffold, it might be responsible for the blue shift observed in our  $\text{CH}_3\text{NH}_3\text{PbBr}_3/\text{Al}_2\text{O}_3$  NPs blends. In order to gain further insights into the origin of the observed PLQY variation, the time-resolved PL was recorded for the same set of samples (Fig 2d). We observed very fast PL decays with lifetimes  $\tau_c$  (the time to reach 1/e of the initial intensity) of 9, 20 and 11 ns for the samples with NPs content of 30, 50 and 75 wt%, respectively, in agreement with the presence of nano-sized perovskite crystallites.<sup>25</sup> The longer lifetime was recorded for the sample with higher PLQY (50 wt% NPs), suggesting a reduction of the nonradiative channels at this concentration.

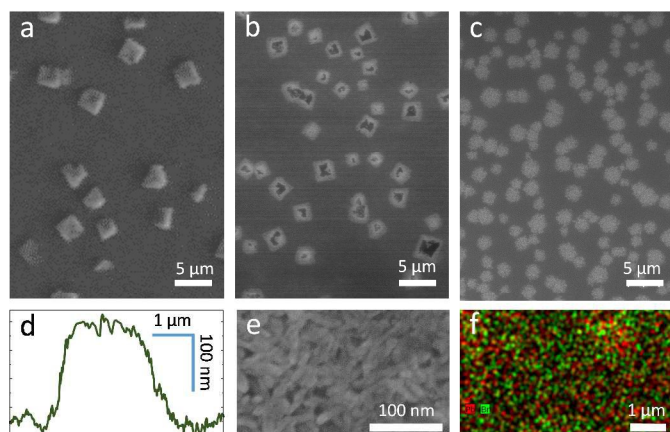


Fig. 3 SEM pictures of the mixed  $\text{CH}_3\text{NH}_3\text{PbBr}_3/\text{Al}_2\text{O}_3$  NPs thin films at 30, 50 and 75 wt%  $\text{Al}_2\text{O}_3$  NPs content (a, b, and c, respectively). (d) AFM profile of a single crystal from a sample containing 30 wt%  $\text{Al}_2\text{O}_3$  NPs. (e) Higher magnification SEM image of the sample surface and correspondent EDXA map for lead (red) and bromide (green).

For a structure-property correlation of the photoluminescence observed in the composite thin films, the material morphology was studied by scanning electron microscopy (SEM). The surface images of the samples with 30, 50 and 75 wt%  $\text{Al}_2\text{O}_3$  NPs content are reported in Fig. 3 (a, b, and c, respectively). Interestingly, we observed the presence of relatively large crystals (diameter of 2–4  $\mu\text{m}$ ) laying on a smooth surface. The profile of a single crystal was measured by atomic force microscopy (Fig. 3d), and found to protrude about 200 nm above the sample surface. A very similar morphology has been recently reported by Li *et al.* when solution processing films from blends  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  with an inert polymer.<sup>20</sup> In our films the system morphology is more complex since the background surface consists of an  $\text{Al}_2\text{O}_3$  mesoporous scaffold observable at higher magnification (Fig. 3e). The composite material contains a large amount of  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  perovskite, as confirmed by the energy dispersive X-ray analysis (EDXA, Fig. 3f). With increasing

$\text{Al}_2\text{O}_3$  NPs content, the formation of the crystals seems to be hindered (Fig S4, supplementary information), finally fading into round aggregates at the highest measured concentration (75 wt%, Fig. 3c). The observed perovskite super-structure on the alumina film is substantially different compared to the often referred to as “capping layer” in the literature.<sup>28</sup> The capping layer is formed when a pure perovskite precursor solution is casted on top of a pre-formed mesoporous metal oxide film, resulting in excess, superficial perovskite growth. While the photoluminescent properties of hybrid perovskites are expected to be morphology-dependent, the large structures observed by SEM images are unlikely the origin of the high photoluminescence observed. The observed blue-shift and the very short PL lifetime is more consistent when originating from perovskite crystals whose size is limited by the alumina NPs scaffold. On the other hand, at low alumina concentration (<30 wt%) the perovskite aggregation within the alumina scaffold is obviously favored and this translates into PL quenching. In order to investigate the morphology of the  $\text{CH}_3\text{NH}_3\text{PbBr}_3/\text{Al}_2\text{O}_3$  NPs composite, transmission electron microscopy (TEM) was performed on powders obtained from scratched films. The TEM analysis (Fig. 4a) shows a morphology in accordance with that observed by SEM (Fig. 3e), where rod-like  $\text{Al}_2\text{O}_3$  NPs assemble forming a dense mesoporous layer.

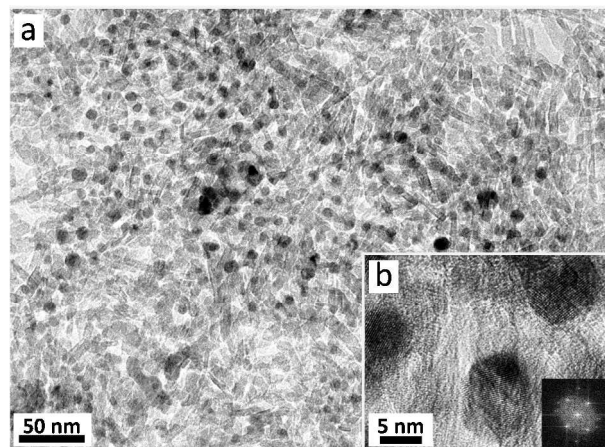


Fig. 4 a) TEM picture of the mixed  $\text{CH}_3\text{NH}_3\text{PbBr}_3/\text{Al}_2\text{O}_3$  NPs thin films at 50 wt%  $\text{Al}_2\text{O}_3$  NPs content at different magnifications. The inset (b) is a HR-TEM image of few isolated NPs with the correspondent FFT.

More interesting is the observation of a high concentration of isotropic nanoparticles with a considerable different contrast. The high resolution TEM (HR-TEM, Fig. 4b) shows that the observed nanoparticles are highly crystalline, and the fast Fourier transform (FFT) of a single nanocrystals confirms the presence of the cubic phase described for  $\text{CH}_3\text{NH}_3\text{PbBr}_3$ .<sup>16</sup> The electron microscopy hence confirms the formation of a nanostructured composite materials where the growth of the hybrid perovskite is controlled and limited by the presence of the alumina NPs, as postulated by analyzing the photophysical properties.

## Conclusions

In summary, high photoluminescence quantum yield  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  perovskite/alumina nanoparticles composite materials have been prepared. A strong enhancement of the photoluminescence as a consequence of the formation of perovskite nanocrystals is observed. The nanocrystal dimensions are governed by the size and concentration of the



alumina nanoparticles. An optimum in photoluminescence was found at a 50 wt% of the alumina nanoparticles at which quantum yields up to 40% were recorded in thin solid films. Furthermore, these materials can be easily processed from solution at low temperature in air and are rather moisture insensitive, making them interesting candidate for future light-emitting and lasing applications.

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### Notes and references

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