Mechanism of the photoluminescence intermittency of hybrid organic inorganic perovskite nanocrystals: the role of the atmosphere

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ABSTRACT:

Lead halide perovskite nanocrystals have demonstrated their potential as active materials for optoelectronic applications over the past few years. Nevertheless one issue which hampers their applicability has to do with the observation of photoluminescence intermittency, commonly referred to as *blinking*, as in their inorganic counterparts. Such behavior, reported for structures well above the quantum confinement regime, has been discussed to be strongly related with the presence of charge carrier traps. In this work we analyze the characteristics of this intermittency and explore the dependence with the surrounding atmosphere, showing evidence for the critical role played by the presence of oxygen. We discuss a possible mechanism in which a constant creation/annihilation of halide-related carrier traps takes place under light irradiation, the dominant rate being determined by the atmosphere.

KEYWORDS: Hybrid organic inorganic perovskites, nanocrystal, photoluminescence, blinking, spectroscopy.

INTRODUCTION:

While their use in photovoltaic applications initially triggered the current interest in hybrid organic-inorganic lead halide perovskites (MAPbX_3 , with X being I, Br or Cl)¹ evidences of their potential as efficient and versatile light emitters have been presented over the past years and this kind of material is widely acknowledged today as a promising component to be integrated in future light emitting devices, from LEDs to lasers.^{2,3,4} Beyond its use as emissive polycrystalline thin films, exploiting the possibility of solution processing the material with outstanding electronic and optical properties, some applications may demand reducing the dimensions of the material. Some examples comprise the use of micro-structures with polygonal shapes which behave as micro and nano-resonators able to provide resonant feedback leading to lasing,^{5,6,7,8,9} or the use of nanoparticles in light emitting applications.¹⁰

An issue when reducing the size of hybrid organic inorganic perovskite crystals is that their emissive properties may undergo changes compromising its use for certain applications. One example comprises the observation of intermittency in their photoluminescence (PL) upon continuous wave illumination as recently observed for MAPbI_3 ^{11,12,13} and MAPbBr_3 ^{14,15,16,17,18} nano and micro-crystals of different size and shape. Contrary to inorganic semiconductors where the presence of such intermittency, commonly referred to as “blinking”,¹⁹ demands the presence of quantum confinement, for hybrid perovskites it has been observed in nanostructures with sizes well above their Bohr’s exciton radius.^{11,12,13,14,15,17,18} As in the case of inorganic nano crystals, where blinking represents a major bottleneck for certain applications such as single-photon emission, understanding the mechanisms behind such changes in the emission is crucial.

In this work we explore the effect of the atmosphere in the PL of individual MAPbBr₃ nanocrystals of 40nm average diameter, which has been reported to play a crucial role in the emission of both nanoparticles (NPs)^{12,16} as well as bulk perovskites.^{20,21,22,23} The NPs present a PL which oscillates between different intensity levels when illuminated over a period of several minutes under continuous wave (CW) excitation. When the atmosphere is changed from air to N₂ and O₂, the PL is seen to be dominated by the lowest and highest PL levels respectively. We propose a picture for this PL intermittency in which an interplay between photo-induced trap creation/annihilation takes place as a consequence of the interaction between the photoexcited NP and the atmosphere.

RESULTS AND DISCUSSION:

MAPbBr₃ NPs were obtained as a sub-product during the synthesis of micron-sized platelets following an already published method (see Methods).⁸ Upon injection of a MAPbBr₃ precursor solution into a dispersion of a surfactant in gamma butyrolactone and further heating at 60°C, a droplet of this resulting dispersion is casted on a zero-fluorescence glass cover-slide. Highly crystalline (see Section S1 and Fig.S1 in the Supporting information) micron sized MAPbBr₃ platelets are found and a distribution of NP is present in the region in between the platelets as evidenced by transmission electron microscopy (TEM) inspection (see Fig.1). Selected area electron diffraction (SAED) patterns of single NP (Fig.1b) shows a high crystalline quality with (001) facets exposed and a measured d-spacing of 2.93 Å to plane (200) as expected for MAPbBr₃. High resolution TEM (HRTEM) images of similar NPs provided identical information

and further confirmed their crystallinity (see Fig.S2). The statistical analysis of size distribution of the MAPbBr₃ NP shows an average size of 39 nm (Figure 1c).

Figure 1. Transmission electron micrograph of a representative MAPbBr₃ NP (a) together with its corresponding SAED (b). Histogram of NP sizes (c) for a collection of NPs like the one shown in the inset. Scale bar corresponds to 500 nm.

Next the luminescent properties of the samples were studied (Fig.2) employing a laser scanning confocal microscope (Zeiss LSM 700 Duo). In an initial study the PL of the sample was collected with a dual CCD which allows retrieving intensity as well as spectral information. When collecting PL intensity (integrated over the 500-590nm spectral interval where MAPbBr₃ emits) the region between the platelets presents a number of bright spots (Fig.2a) with an average size (202 ± 48 nm) close to the diffraction limit where the instrument is expected to operate (189nm). The spectrum of individual NPs was retrieved and fitted to a Gaussian curve (Fig.2b) centered at 532nm where emission for bulk MAPbBr₃ is expected. This is in agreement with the fact that the NP

average size is an order of magnitude larger than the Bohr's exciton radius for this material (2nm),²⁴ and thus no quantum confinement effects are expected.

Figure 2. (a) Spatial profile of the PL of a NP. Inset shows a typical PL image of a region containing several NP. Scale bar corresponds to 2μm. (b) Experimental PL spectrum of a NP (circles) and fit to a Gaussian curve (line). (c) Time trace of the PL of a NP. Gray curve shows the background PL.

When observed under CW illumination the individual NP showed PL intensity intermittency, similar to the blinking observed in semiconductor nanostructures (Fig.2c). In order to trace the temporal evolution of the PL images a high-speed camera was used (LSM 5 Live from Zeiss) which allowed us to collect time series of PL images of distributions of NPs with 33ms steps. After that we can analyze the PL evolution of individual NPs. Contrary to conventional PL blinking in inorganic QDs, which usually

presents a “binary” behavior where the PL oscillates between an ON and an OFF state, the intermittency in our NPs oscillates between a number of discrete PL levels (see Fig.S3 and Section S2a in the Supporting Information), where for most NP examined this number was three. The presence of such intermediate “grey” levels accompanying the usual ON/OFF states has been recently observed in inorganic QDs and associated with the presence of charged trions showing a different quantum yield from that of the exciton.^{25,26} In our experiments the observed PL intermittency begins upon illumination without any gradual increase in PL intensity. Such gradual photoactivation has been reported in the past for MAPbBr₃ QDs¹⁶ and MAPbI₃ micro-crystals^{11,13} and related with trap filling which would eventually prevent blinking. Here the intensity of the OFF and ON states was observed to remain constant over several minute-long measurements. Further, no spectral change in the NP PL was observed during its transition from one PL intensity level to another (see Fig. S4 and Section S2b in the Supporting Information). Finally, duration statistics were extracted for the different PL intensity levels and an inverse power law was retrieved in all cases (see Fig. S5 and Section S2c in the Supporting Information) showing the absence of a characteristic time in the PL intermittency as in the case of inorganic QDs.

Next the effect of the atmosphere in the observed behavior was taken into account, as it has been demonstrated that it strongly influences the PL from bulk hybrid organic inorganic perovskites^{20,21,22,23} as well as the blinking behavior from NPs.^{16,12} Further, for inorganic semiconductor QDs the role of the surrounding atmosphere has also been reported to determine their blinking statistics.^{25,27} Fig.3a-c shows the time evolution of the PL of a NP under different atmospheres together with the corresponding count rate histograms (Fig.3d-f). For the case of NP in ambient air the histogram (Fig.3d) clearly shows three peaks which correspond to the ON, OFF and gray PL levels already evident

from the PL time evolution graph (Fig.3a). Upon exposure of the NP to an O₂ atmosphere, the PL time trace abruptly changes (Fig.3b). To better compare this behavior with that of the NP in air we can extract the count rate histogram (Fig.3e). Here again three PL levels can be observed which do not exactly match in position with those in air. What can be clearly observed is the fact that the NP spends more time in the ON state as compared with the results in the air atmosphere. On the contrary, when exposing the NP to N₂ the PL time trace undergoes an additional change (Fig.3c) and the NP's PL is depleted showing nearly no counts, close to the background (BG) level (Fig.3f). Finally, no difference was found between time traces in dry and ambient air (relative humidity RH $\approx$ 30%) indicating that, at least within this RH range, moisture plays a negligible role in the PL of the NPs which is mainly dictated by the gas species forming the surrounding atmosphere.

Figure 3. (a-c) Time evolution of the PL of a NP under three different atmospheres: air (a), oxygen (b) and nitrogen (c). Grey curve represents the background PL for each

measurement. Panels (d-f) show count rate histograms for the same atmospheric conditions.

In inorganic colloidal QDs non-radiative Auger recombination in charged NP is commonly regarded as the mechanism behind PL intermittency. This multi-particle process, while being highly inefficient in bulk semiconductors, becomes more probable in the presence of quantum confinement due to a relaxation in translational momentum conservation. This is associated with the fact that the efficiency of the process presents a linear dependence with the QD volume, the so-called “V-scaling”,^{28,29} which causes a reduction in the Auger constant upon decreasing the QD size. In the present work the NP sizes for which intermittency in the PL is being reported is an order of magnitude above the Bohr’s exciton radius for this material²⁴ and thus quantum confinement effects are not observed, as mentioned above. Hence, we can expect a bulk behavior in terms of Auger recombination processes and, due to the low pump intensity employed in our experiments (0.2 W/cm^2), a marginal contribution of such processes. This further evidences the different origin of PL intermittency in the present, and most of the reported lead halide perovskite systems, from that of inorganic QDs. For the latter the presence of discreet energy levels and a localized exciton arising from quantum confinement is required. For the case of hybrid perovskites, for which a bulk behavior of its PL is expected, several works have pointed crystalline defects as the origin for PL intermittency.^{11,12,13,16} In this direction and in an effort to enhance the emission properties of nanostructured MAPbBr₃ films and the performance of light emitting devices made from them some studies have shown how such films underwent an improvement in their PL accompanied by a reduction in blinking when treated with amines (to reduce crystalline defects acting as non-radiative recombination centers)

either as a post-process treatment¹⁷ or during its synthesis.¹⁸ Lewis bases have also been used as a means to passivate the surface of MAPbBr₃ NPs to enhance its emission.¹⁶

In order to understand the reported intermittency and its dependence on the surrounding atmosphere, we will first discuss the different mechanisms which can lead to enhanced/decreased PL in our MAPbBr₃ NPs. For the particular case of MAPbX₃, the atmosphere plays a decisive role in the PL. It has been demonstrated that in the presence of inert gases^{20,22,30} or vacuum,^{22,23} the PL is severely quenched with respect to other atmospheres (see below). This behavior, which was initially attributed to the formation of photogenerated defects of unknown nature,³⁰ is likely related with the formation of halide vacancy/interstitial pairs due to an enhanced ion mobility in the presence of light irradiation as recently demonstrated by Maier and co-workers.³¹ In this sense it has been shown that bromine vacancies can introduce deep trap states in the bandgap of MAPbBr₃ which can act as non-radiative recombination centers and thus quench the PL of the material.³²

Regarding the photoactivation of hybrid organic inorganic perovskites, where the PL of the material undergoes a monotonic increase under continuous optical excitation, reports have been presented for both MAPbI₃^{33,20,21} and MAPbBr₃^{22,23} as well as evidence showing the role of the atmosphere on the process.^{20, 21, 22,23} While there is general consensus on the fact that such increase in PL is due to the de-activation of carrier traps responsible for introducing non-radiative carrier recombination paths and thus quenching the material emission, there is an ongoing debate on the precise nature of such traps and the driving force behind the passivation.

Experimental evidence was provided by De Quilettes and co-workers that the PL activation was accompanied by a redistribution of the halide component upon

illumination of MAPbI₃ polycrystalline films.³⁴ A similar redistribution of the halide distribution in MAPbBr₃ single crystals accompanying PL redistribution was also reported.³⁵ First principle calculations have also shown that light irradiation can lead to the annihilation of halide-related Frenkel-pairs present in the perovskite matrix.³⁶ These two observations are, in principle, compatible with the above mentioned photogenerated enhanced ion mobility.³¹ However these mechanisms do not tackle the widely acknowledged role of oxygen in the photoactivation of halide perovskites. In this direction two recent reports have pointed out how this gas can help to improve the material photoluminescence quantum yield (QY), either by penetrating the perovskite lattice and de-activating deep traps associated with halide interstitials in MAPbI₃³⁷, or by creating a negatively charged layer of superoxide on the MAPbBr₃ crystal surface which provides a driving force for the displacement of bromide ions and will eventually lead to material degradation.²³

In view of these considerations we propose a mechanism for the observed PL intermittency in which a number of traps associated with halide vacancies/interstitials are being constantly generated/annihilated under external CW illumination, the dominant rate depending on the surrounding atmosphere. When irradiating the NPs in air, a competition between the two mechanisms takes place and traps are being populated/depopped leading to the observed intermittency of the PL (Fig.3a). In an inert atmosphere light irradiation mainly leads to the formation of traps causing the MAPbBr₃ NP to remain most of the time in an OFF state when excited with CW light (see Fig.3c), in agreement with the reports for bulk MAPbI₃³⁰ and MAPbBr₃.²³ When the atmosphere is changed to dry oxygen, the combined action of its incorporation in the lattice³⁷ and the formation of a negatively charged surface layer²³ promotes the passivation of deep traps, the latter taking place via the migration of bromine

interstitials towards vacancies, and increases radiative recombination of photogenerated carriers (Fig.3b). The time duration of this PL intermittency process, in the order to tens of seconds, further points to an origin related with ionic motion. The presence of a finite number of defects is in accordance with recent reports^{38,39} where the defect density for MAPbBr₃ crystals of different size has been estimated employing optical techniques leading to values in the 10¹⁴-10¹⁵ cm⁻³ range, which would indicate the existence of 0.1-1 defects per NP in our case. While this value is slightly below the observed number of PL levels, our synthesis differs from those in refs. 38 and 39 which could explain a slightly larger defect density.

Opposite to the bulk material, where PL quenching when illuminated under an inert atmosphere is reversible,^{22,30} for the case of NPs we observed that PL does not recover after prolonged illumination in N₂ and posterior restoring an O₂ or air atmosphere (see Fig.S6 and Section S3). This indicates that for samples of such reduced dimensions, orders of magnitude below the bulk materials reported before, the defects generated upon the photo-induced enhanced ion mobility lead to the degradation of the crystalline lattice within a few minutes. Further it shows that the presence of O₂ in the surrounding atmosphere prevents this irreversible degradation since, beyond promoting the ON states during PL intermittency, it maintains the different PL levels constant in time. In a former report by Yuan and co-workers¹² the role of oxygen in the blinking of MAPbI₃ nanorods was not isolated as they only studied the PL in the presence of inert atmosphere and air, and thus related the activation of the PL to the presence of O₂ and water leading to the passivation of under-coordinated lead at the surface.

Finally a comparison with inorganic QD, for which the atmosphere has also been demonstrated to play a relevant role,^{25,27} can be made. While some similarities exist such as an overall PL reduction upon exposure to vacuum or inert atmospheres, the role

of oxygen has either not been isolated²⁵ or demonstrated to introduce only large PL changes combined with the presence of water.²⁷ Further, for the case of inorganic QD a lower ion mobility is expected so that the mechanism leading to modification of the PL intermittency is more likely related with the modification of the sample surface.

CONCLUSION:

We have studied the time evolution of the PL of MAPbBr₃ NPs with average sizes of 40nm, far from the regime where quantum confinement effects are expected. The emission from these NPs presents intermittency between different intensity levels when observed over time under CW optical excitation. The characteristics of this intermittency are strongly dependent on the atmosphere surrounding the NP, as is the case with the bulk material. In particular when exposed to O₂ the NP spends most of its time in the highly emitting levels while exposure to N₂ drops the PL close to the BG level of the measurements. Based on these data and recent previous reports for this material we propose a mechanism for this intermittency in which an interplay takes place between trap creation/annihilation under illumination, where the dominant rate is determined by the surrounding atmosphere. This mechanism, which involves the migration of halide ions within the interior of the NP is likely happening in parallel with charge trapping by surface defects as suggested by previous works where surface passivation reduced the intermittency of blinking. As blinking poses a serious limitation for the application of these NP, as it reduces the overall material QY, these results could offer a path towards the improvement of the luminescent properties of the material, such as introducing a post-processing treatment based on illumination in the presence of oxygen and posterior encapsulation of the material.

METHODS:

Sample preparation: MAPBr micro structures were fabricated following an already published procedure.⁸ The method consists in the rapid addition of 30 μl of a 35% (w/w, total) solution of MABr and PbBr_2 (1:1 molar ratio) in N,N-dimethyl formamide to 1 ml of 0.25mM solution of dodecylammonium bromide in gamma-butyrolactone. After mixing, the solution is heated at 60°C during 20 minutes without agitation. A 40 μl of the supernatant is taken and deposited onto cover microscopy slides (Carl Zeiss, 170 μm thick) previously cleaned. Finally, these samples are treated in a stove at 100° during 30 minutes.

TEM characterization: For TEM inspection a drop of the original NP suspension was deposited on a grid coated with a holey carbon film. The transmission electron images were obtained with a microscope (Philips CM20) with fast operation at 200 kV in order to prevent material degradation.

Optical characterization: The luminescent properties of the NP were studied with a commercial LSCM (Zeiss LSM 700 Duo) using a high N.A. oil-immersion objective (Plan-Apochromat 63x, NA=1.4). The illumination was performed with a CW diode laser operating at 488nm and a power of 0.2W/cm². The system has three detection paths comprising a conventional PMT (for collecting PL intensity), an additional PMT allowing for spectral information (with variable spectral resolution of 4.9nm or 9.8nm) and a high-speed camera (LSM 5 Live from Zeiss). For recording the time evolution of the luminescence of sets of NP the spectral PMT or the high-speed camera were used depending on whether spectral information was needed.

ASSOCIATED CONTENT:

The Supporting Information is available free of charge on the ACS Publications website.

Characterization of PL intermittency (Blinking traces for different NP; Spectral properties of NP; Probability distributions), dependence of blinking on the surrounding atmosphere. (PDF)

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