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Interplay between connectivity and passivating agents in perovskite quantum dot networks†

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Introducing quantum dots (QDs) as the active element of an optoelectronic device demands its incorporation in the shape of interconnected arrays that allow for some degree of electronic coupling in order to inject/extract charge carriers. In doing so, beyond reducing the degree of quantum confinement, carriers are exposed to an enhanced defect landscape as they can access adjacent QDs, which is at the origin of the strong reduction of photoluminescence observed in QD solids when compared to that of the isolated QDs. In this work we demonstrate how a proper defect passivating strategy or atmospheric treatment can greatly enhance charge diffusion in a QD film, needed for an optimal carrier injection/extraction demanded for optoelectronic applications, and also improved its stability against external radiation. From a fundamental perspective, we provide evidence showing that trap density distribution, rather than QD size distribution, is mostly responsible for the observed variations in emission decay rates present in the QD networks under analysis.

perovskites.⁷ The choice of the A cation has strong implications on the material stability and can further contribute to reduce structural defects acting as charge traps or affect the electronic bandgap edges.⁸ Replacing methylammonium (MA) in the prototypical formulation MAPbI₃, employed for record photovoltaic devices in the initial stages of the field, with formamidinium (FA) allowed for a material with enhanced thermal stability and a bandgap close to the optimum value of the Shockley–Queisser limit. This has led to FA-based photovoltaic devices with record efficiencies over the past few years.^{9–11} Recently, it has been shown that the Br-containing counterpart FAPbBr₃ presents a high phase, moisture and temperature stability,¹² along with high photoluminescence (PL) quantum yield (QY), particularly when synthesized in the shape of quantum dots,¹³ which has risen the interest in this material for light emitting applications.

When used in solar cells or light emitting diodes (LEDs), semiconductor QDs must be incorporated in the shape of films, in which a certain degree of electronic coupling between the QDs is necessary to allow for charge injection and transport.¹⁴ Among the different routes to fabricate such QD ensembles, ligand-free synthesis within the pores of nanoporous metal oxide matrices has been recently demonstrated as a suitable approach to prepare HP QD films with optical quality and versatility regarding QD size, composition and concentration.^{15–20} When deployed as films, the recombination properties of QD undergo pronounced changes and a bulk-like or isolated QD-like behavior is present depending on QD connectivity.²¹ The presence of structural defects strongly affects recombination in QD films as photogenerated carriers have access to a larger defect landscape since they can diffuse across many QDs.

In this work we study the role of crystalline defects in charge carrier recombination of ligand-free FAPbBr₃ QD films grown within metal oxide nanoporous matrices. In order to evaluate the effect of defects of different nature we explore polymeric encasement, which has been recently shown to act as efficient surface trap passivators,²² as well as different environmental agents which are known to interact with the defect structure of lead halide perovskites.^{23,24} These results are interpreted in the

1. Introduction

Over the past decade, halide perovskites (HPs) have emerged as a family of semiconductors with potential for applications in diverse fields from photovoltaics,¹ light emission,^{2,3} photocatalysis⁴ or radiation detection⁵ having achieved state-of-the-art performances in many cases. An appropriate choice of precursors allows for attaining conventional three-dimensional (3D) perovskites having the chemical formula ABX_3 (with A being a monovalent cation, B a bivalent metallic cation and X a halide anion), low-dimensional structures comprising n -dimensional inorganic films separated by large organic molecules⁶ or other structures such as double

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light of recent literature dealing with the defect structure of FA-based HPs and the role of different trap states in carrier recombination is discussed. We demonstrate how a proper defect passivating strategy can greatly enhance charge diffusion in a QD film, needed for an optimal carrier injection/extraction demanded for optoelectronic applications, and also improved its stability against external radiation. From a fundamental perspective, we provide evidence showing that trap density distribution, rather than QD size distribution, is mostly responsible for the observed variations in emission decay rates present in the QD networks under analysis.

2. Results and discussion

2.1 Bare QD films in an inert N₂ atmosphere

FAPbBr₃ QDs were synthesized within the pores of nanoporous SiO₂ films (see Fig. 1a) following an already published procedure,²² detailed in the (ESI†). These samples, labeled FAPbBr₃@SiO₂, were kept in an air-tight chamber through

which different gasses can be flown. Initial measurements were performed in a N₂ atmosphere. By increasing the precursor concentration (C_{prec}), we are able to enhance the connectivity between the QDs embedded within the porous scaffold, since the average inter-QD separation is reduced as we increase their number density.²¹ This approach also implies a rise of the average NC size, as it can be seen in Fig. 1b and c, where a reduction in precursor concentration leads to a blueshift in both the absorption edge and PL peak, as expected for NC sizes falling within the quantum confinement regime (estimations for average QD size and separation are given in Table S1 of the ESI†). It is also observed that the average QD separation affects the photoluminescence (PL):^{21,22} the higher the connectivity, the lower the PL intensity measured from FAPbBr₃@SiO₂ samples excited under identical irradiation conditions (see Fig. S2 in the ESI†). Such drop cannot be explained only in terms of a reduced quantum confinement for larger QDs. As QDs get closer, electronic coupling allows charges to diffuse across different QDs, thus expanding the defect landscape they have access to, leading to a reduced PL QY.^{21,22} This is further



Fig. 1 (a) Scheme of a QD array grown within a SiO₂ nanoporous matrix (left), TEM image of a sample infiltrated with a 20% precursor solution (middle) and PL image of a real sample under UV illumination (right). (b) Absorption (normalized at $\lambda = 475$ nm), (c) normalized PL, (d) PL decays for high (3 μ W, dark curves) and low (30 nW, light curves) and (e) evolution of PL under CW irradiation for samples with different precursor load/interparticle separation. Color code is the same for all four panels: 5%/28 nm (blue), 10%/22 nm (green) and 20%/15 nm (red curve).



occurring in the bulk of the larger QDs, which emit in the longer wavelength region. For the case of connected QDs (Fig. S4c, ESI⁺), PL quenching is less pronounced and does not involve spectral changes. The latter agrees with the fact that, for QD arrays, PL is expected to come from those QDs with smaller bandgap after a carrier diffusion process following the energy landscape of the array. The photostability of FAPbBr₃ has been dealt with only recently²⁶ for macroscopic single crystals where a bulk reversible PL darkening was observed and associated with the perovskite lattice decomposition upon irradiation. In such process, byproducts in gas phase can recombine with other byproducts leading to the re-composition of the lattice. The possible origin of our findings will be further discussed when results for different treatments are dealt with.

To gain further insight into the role of structural defects on both the carrier transport in QD films as well as on the observed photo-instability, we next consider identical samples to the ones discussed above, but with the remaining empty volume of the nanopores infiltrated with poly(methyl methacrylate) (PMMA) after FAPbBr₃ QD synthesis (labeled as FAPbBr₃@PMMA@SiO₂) (see fabrication details in ESI[†]). This approach, expected to act on surface traps, has been observed in the past to lead to defect passivation and improved PLQY on similar samples.²² These results are in line with recent *ab initio* studies for FAPbI₃, which have shown that, while bulk defects are expected to be more abundant in this material due to a lower defect energy formation,²⁷ only surface defects occurring for some terminations are expected to introduce deep traps that

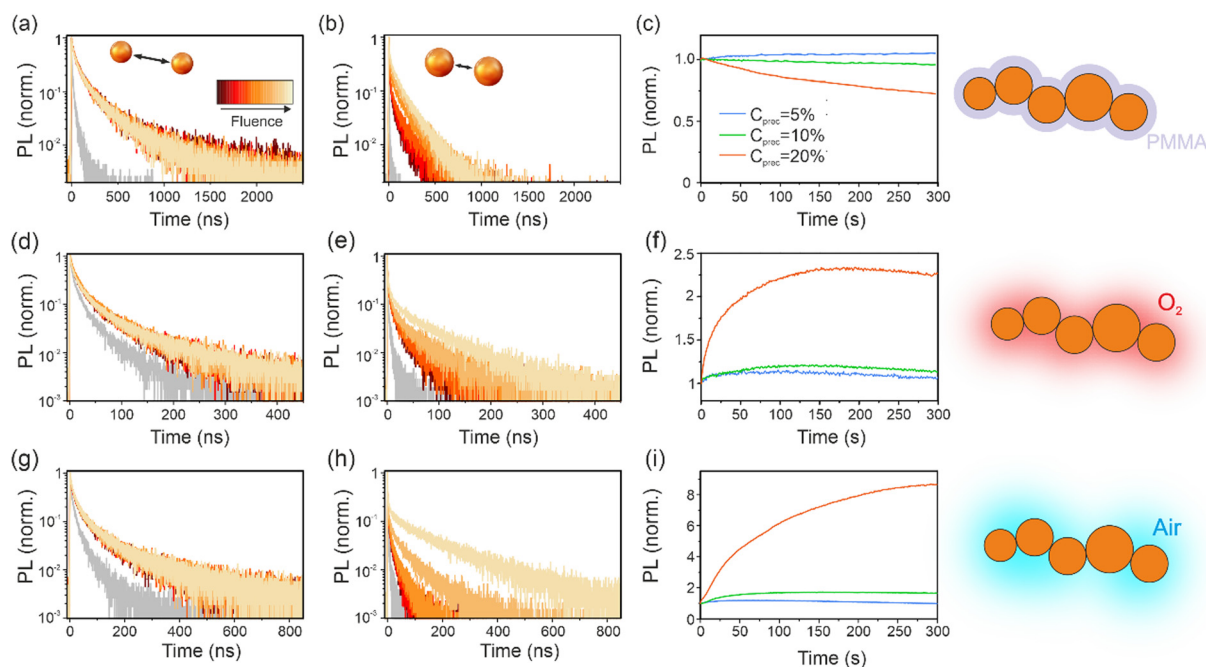


Fig. 2 TRPL for samples with (a) low ($C_{\text{prec}} = 5\%$) and (b) high ($C_{\text{prec}} = 20\%$) connectivity infiltrated with PMMA. (c) Time evolution of PL under CW irradiation for the three different samples under study: $C_{\text{prec}} = 5\%$ (blue), $C_{\text{prec}} = 10\%$ (green) and $C_{\text{prec}} = 20\%$ (red curve). (d)–(f) and (g)–(i) show identical data for bare samples exposed to O_2 and humid air respectively. In all cases, the TRPL data for the same samples in N_2 are plotted as grey curves for the sake of comparison.

The diagram illustrates a polymer chain (represented by orange circles) with various defects and traps. A legend on the right defines the symbols: a white square for 'Trap', a hatched square for 'Passivated Trap', a black dot for 'Hole', and a grey circle for 'Electron'. The top part of the diagram shows a segment of the chain with several traps and a hole. A blue wavy arrow labeled 'Pump' points to the left, indicating the direction of excitation. The bottom part shows a similar segment, but with passivated traps (hatched squares) and a green wavy arrow labeled 'PL' (Photoluminescence) pointing to the right, indicating the emission of light. The label 'PMMA' is at the bottom right.

taking place (see Fig. 2c). The fact that irreversible degradation is now absent for this sample indicates that surface traps, beyond acting as deep traps leading to the quenching of PL, also represent seed points where degradation is triggered. For the case of the samples with higher precursor load where QD interconnectivity is expected ($C_{\text{prec}} = 20\%$) we now observe a photo-induced PL darkening that is reversible when CW irradiation is removed (see Fig. S6, ESI[†]). Two types of mechanisms have been reported for reversible photodarkening in HPs. A decomposition of the HP lattice into its precursors and further formation of gaseous byproducts was invoked in ref. 26 as the process leading to reversible darkening of FAPbBr₃ single crystals when excitation is performed in the bulk and byproducts cannot escape the crystal. If this mechanism was behind our observations, PL darkening should be observed for all QD films regardless of their load. On the other hand, Motti and co-workers proposed²⁹ the formation of I₂ upon annihilation of halide-related Frenkel pairs as a possible origin for PL quenching. This would explain the present results in the event that halide defects could migrate across different QDs in our interconnected samples. Br₂ forming as a result of the annihilation of Frenkel pairs could not escape the film due to the presence of the PMMA film and the process could be reversed upon removing the CW irradiation.

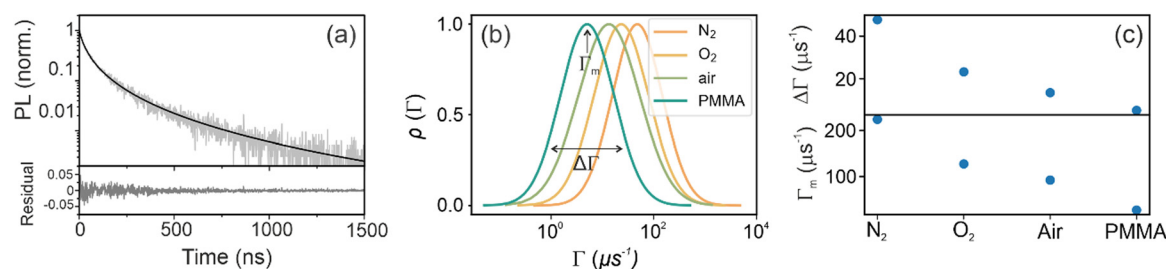
Next, we consider the surrounding atmosphere as a treatment with potential to modify the defect landscape in $\text{FAPbBr}_3@\text{SiO}_2$ samples. The role of the environment on HP photophysics and stability has been extensively studied over the past decade. There is nowadays a consensus that certain gases can strongly modify the defect landscape in LHP at the expense of reducing material stability so that a compromise must be attained if one wants to employ this approach to optimize their optoelectronic properties.^{30,31} In this work we have explored the role of O_2 and moisture. We first exposed our sample to a continuous flow of dry O_2 (<3 ppm background humidity according to the provider, Linde) for 5 minutes prior to study their optical properties. Time resolved photoluminescence (TRPL) data shows a slight slowing in the PL decays for all samples under study (Fig. 2d and e). This is likely related with the interaction of O_2 with a certain population of deep traps, as evidenced by the fact that TRPL becomes again fluence dependent for the highly connected sample. This interaction takes place *via* weak binding of O_2 to FAPbBr_3 (physisorption) as the effect is rapidly reversed upon restoring a N_2 atmosphere.

More evident changes appear when the effect of O_2 is combined with that of CW irradiation and we monitor the sample PL (Fig. 2f). Here we can observe that samples with small connectivity barely experience any change in their PL but highly connected samples undergo a >2 fold enhancement, pointing to the photoinduced interaction of deep traps with this reactive atmosphere. As with the case of samples infiltrated with PMMA, no spectral changes were observed for the highly connected samples (Fig. S7, ESI⁺). While reports on the interaction of O_2 with FAPbBr₃ are lacking, recent evidence showing emission changes of other MA-based HP may hold the key to explain the present results. In particular, a photoinduced PL rise in the presence of O_2 has been previously reported^{32–38} and

surrounding atmosphere is expected to be the same for all different samples, the photoinduced PL enhancement is more pronounced for the case of connected QDs. The reason behind this observation is the stronger effect of traps on the sample emission for connected QD arrays (see Scheme 1), where a larger defect landscape arises as a consequence of carriers being able to diffuse across several QDs. To evaluate and quantify the role of the different treatments, we consider the $C_{\text{prec}} = 5\%$ samples, *i.e.* those having the lowest connectivity, where fluence does not play a role in the emission. We compare the PL decay under different atmospheres as representative of the weight of non-radiative processes. To extract a parameter for comparison we fit the TRPL to a lognormal distribution of decays, $\rho(\Gamma)$ (see Fig. 3a for the FAPbBr₃@PMMA@SiO₂ sample, and Fig. S10 (ESI[†]) for FAPbBr₃@SiO₂ exposed to different atmospheres). As previously reported,²¹ the mode of the distribution (Γ_{m}) represents an average value of the decay rate of the distribution of QDs. The width of this distribution will be affected by the size dispersion but could also be influenced by the defect distribution in different QD. From the comparison of all Γ_{T} it becomes clear that the treatment that more efficiently de-activates deep traps is that of PMMA (Fig. 3b), further highlighting the detrimental role of surface defects in this material. Additional information can be extracted from a comparison of the actual decay rate distribution for QD films in N₂ and with the different treatments (see Fig. 3c). The average value of the decay rate distribution Γ_{T} comprises a radiative (Γ_{R}) and a non-radiative (Γ_{NR}) component. While the former is assumed to be identical for all samples, the latter depends on the defect landscape as:

$$\Gamma_{\text{NR}} = \sigma_{\text{trap}} v_{\text{th}} N_{\text{T}}$$

Hence the non-radiative recombination is directly affected by the number of trap sites in the system, (N_{T}) their capture cross section (σ_{trap}) and the thermal velocity of the free charge carriers (v_{th}), the latter remaining unchanged for the different treatments. The reduction of the number of trap sites can be explained as halide related defects interact with environmental gas molecules, while a change in σ_{trap} can be assigned to a change in the energy level of a trap state, such as the one predicted for interstitial iodide in the presence of O_2 .⁴¹ To shed



J. Mater. Chem. C, 2024, 12, 16683–16690 | 16687

more light into the exact origin of the reduction in Γ_{NR} , the distribution of recombination rates is analyzed in the following. Here it can be seen that adding the polymer as a passivating agent not only reduces the average decay rate, evidencing the reduction of non-radiative recombination paths, but also homogenizes the PL dynamics of the QD distribution as its width is reduced by an order of magnitude (Fig. 3c). This latter fact further evidences that trap density distribution, rather than size distribution, is mostly responsible for the observed variation in decay rates in the present QD films.

The distribution of decay rates can be associated to both the non-radiative (Γ_{NR}) and radiative (Γ_{R}) components, where non-radiative components are expected to show both larger decay times and a broader distribution of decay times. As the different treatments (atmosphere and PMMA) are acting on the sample, a reduction of the decay rate distribution is observed (Fig. 3c). The continuous decrease of both the average values of the distribution and its width is observed as surface defects interact with one of the abovementioned agents. Since both parameters decrease in the same monotonic way, the global reduction in decay rates can be solely assigned to the reduction in the number of trap states. A significant change in the distribution of defect states would involve a more drastic change in the width $\Delta\Gamma$, rather than in the mean rate Γ_{m} . Further, an assignment of the broad distribution to a size and energy dispersion due to the heterogeneity of the crystals is discarded, as in this case, $\Delta\Gamma$ and Γ_{m} would not follow identical dynamics.

3. Conclusions

In summary, we have explored the role of defects in charge recombination for HP QD films using ligand-free QDs fabricated within the pores of silicon oxide matrices. The use of different treatments evidences that surface traps are a main source of non-radiative recombination in FA-based HP and its presence constitutes a burden for carrier transport in QD films. Thus, a proper passivation approach represents an efficient avenue for avoiding this issue and improving the performance of devices containing these materials. Further, surface traps have also been shown to represent a source of instability leading to irreversible material degradation in the absence of appropriate passivation. Finally, we have presented the first evidence of photo-induced PL activation in FA-based HP as a consequence of the combined action of irradiation and exposure to reactive atmospheres. This latter effect is mainly related with defect reactivity at the HP surface and thus previous reports dealing with larger samples could not observe it.

Data availability

The data underlying this study are openly available in the Digital CSIC repository: <http://hdl.handle.net/10261/368936>. The codes used to fit the TRPL data are provided at <https://github.com/Multifunctional-Optical-Materials-Group>.

Conflicts of interest

There are no conflicts to declare.

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