Monitoring, Modelling and Optimization of Lead Halide Perovskite Nanocrystal Growth within Porous Matrices

David O. Tiede^{†‡}, Andrea Rubino[‡], Mauricio E. Calvo, Juan F. Galisteo-López, Hernán
Míguez**

Instituto de Ciencia de Materiales de Sevilla (Consejo Superior de Investigaciones Científicas-
Universidad de Sevilla). C/Américo Vespucio 49, 41092 Sevilla (Spain).

Corresponding Authors

* Professor Hernán Míguez, h.miguez@csic.es

* Dr. Juan F. Galisteo-López, juan.galisteo@csic.es

† Current address: Westfälische Wilhelms-Universität Münster, Wilhelm-Klemm-Str. 10, 48149
Münster (Germany).

‡ These authors contributed equally.

ABSTRACT

The growth of lead halide perovskites within metal-oxide nanoporous films has been recently considered as a means to obtain chemically and photo-stable ligand-free high quality nanocrystals. The growth process, governed by the reactions taking place in nano-reactors dictated by the matrix pore size, has not been explored so far. In this work we use photoluminescence as a tool to monitor the growth of perovskite nanocrystals within the void network of an optically transparent matrix. We consider the effect of different external factors, such as temperature, light illumination or precursor concentration, on the growth dynamics, and discuss a possible formation mechanism of the confined perovskite nanocrystals. Based on this analysis, guidelines that could serve to improve the fabrication and optoelectronic quality of this type of nanocrystals are also proposed.

Introduction:

The possibility of tuning the optical and electronic properties of semiconductor nanocrystals (NCs), having dimensions on the order of the exciton Bohr radius, via their size and morphology has inspired intensive work over the past three decades. Part of the interest in these so-called quantum dots (QDs) comes from the possibility of incorporating them as active elements into optoelectronic devices.¹ But prior to the transition from materials, such as semiconductor QDs, to commercial devices one needs to exert a precise control on their properties (determined by their size, shape, composition and quality) and stability, as well as to provide a reproducible fabrication procedure. In this sense a great effort has been put over the past two decades into understanding the growth mechanism of QDs.² This has led to a deeper understanding on the different parameters affecting their nucleation and growth such as precursor composition, temperature, the role of organic ligands, etc.

The past few years have seen the rise of a new direct-bandgap semiconductor material which can be solution processed from earth-abundant materials and with outstanding properties for optoelectronic applications, namely lead halide perovskites (LHP). The interest in this family of materials was initially triggered by their performance as active components for photovoltaic devices which have shown to be the fastest growing solar cell technology so far, with a rise in efficiency departing from a few percent³ to values pairing those of commercial silicon cells in

less than a decade.⁴ Also, as with conventional III-V and II-VI semiconductors, reducing the size of LHP NCs down to their exciton Bohr radius allows for a precise tuning of their bandgap, which may be highly relevant for optoelectronic applications.⁵ Indeed, LHP NCs offer additional advantages with respect to conventional QDs in the form of bandgap tunability through their composition or an unusually high tolerance to structural defects.^{6,7} Understanding the synthesis is a crucial step towards the commercialization of these NCs. In this respect a number of works have dealt with the growth mechanism of LHP colloidal NCs focusing on different aspects such as precursor ratios, synthesis temperature or the presence of ligands,⁸⁻¹⁵ as a means to rationalize their production. As an alternative to the widespread use of colloidal synthesis, several approaches have been recently proposed where LHP NCs are grown within metal-oxide mesoporous matrices which pore structure serves as nano-reactors for the growth of the NCs.^{6,16,17-23} This allows for the production of NCs with controlled size and well isolated from each other presenting photoluminescence (PL) quantum yields (QYs) close to those of their colloidal counterparts and a photo-stability, one of the main limitations of LHP, greatly improved with respect to the bulk materials. Further, this synthetic approach allows for the growth of NCs directly into a transparent solid matrix without any loss in emission efficiency. This has led to demonstrations, when using an appropriate metal-oxide matrix, of solar cells²¹ and light emitting diodes²² which, albeit presenting efficiencies below the state-of-the-art values in the field, are promising proofs of concept. Finally, the fact that the NCs are grown free from the organic ligands needed to stabilize their colloidal counterparts, allows studying the intrinsic properties of the material as a function of its size.

Profiting from the possibility of using highly transparent mesoporous films for the synthesis of these NCs, we have followed the growth of LHP NCs inside these matrices. Using PL

measurements we can perform an in-situ study of the growth kinetics of a fixed population of methylammonium lead bromide ($\text{CH}_3\text{NH}_3\text{PbBr}_3$) NCs, thus having access to the early stages of the process. For the case of NCs grown in solution these studies require either the use of aliquots extracted from a base reaction solution or introducing microfluidic adaptations to the process.^{9,11} Please note that, in either case, the same population of NCs cannot be studied throughout the entire process. Herein we evaluate the effect of different factors affecting the synthesis such as external illumination, temperature or precursor concentration, as well as proposing a formation mechanism and find the optimal conditions for NC growth.

Experimental Methods:

Sample Fabrication: Nanocrystals were synthesized following a procedure reported elsewhere that allows growing, within a porous matrix made of silica nanoparticles (NPs), a collection of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ nanocrystals presenting a narrow size distribution and displaying strong quantum confinement effects.^{20,23} Thin (ca. $1\mu\text{m}$) films of a nanoporous SiO_2 matrix were fabricated by dip-coating a glass substrate into a SiO_2 -NP dispersion in methanol according to a previously described method. Next the nanoporous film was infiltrated with a perovskite precursor solution prepared by dissolving MABr and PbBr_2 (3:1 molar ratio) in DMF. In order to obtain a homogeneous distribution of perovskite NCs throughout the sample but still analyze the early stage of NCs growth, the solution was deposited by spin coating on top of the porous matrix at 5000rpm for 10s. The film infiltration was performed in a glove box under inert atmosphere and then taken outside for optical characterization. For those measurements demanding a reference measurement the sample was cut into two right after spin coating and before taking it out of the

glovebox. Figure 1(a) displays the characteristic X-ray diffractogram of these NCs, along with TEM pictures of a cross section of the inner walls of the host decorated with nanocrystals of well-defined size at different magnifications in Figures 1(b) and (c).

Optical Characterization: The optical properties of mesoporous films made from 30nm SiO₂ NPs and infiltrated with a solution of CH₃NH₃PbBr₃ precursors in dimethylformamide (DMF) were tracked with time to obtain information on LHP-NC growth. SiO₂ NP films were infiltrated with the LHP precursor solution in an inert atmosphere within a glovebox by spin coating. The films were extracted from the glovebox and placed in an adjacent optical set-up where PL spectra were collected during 100s of minutes until the NC growth was completed, as evidenced by a stationary behavior of the PL peak (see Table S1 in the Supporting Information for the illumination pattern). Spectra were measured by focusing a pulsed laser beam (900ps pulse duration, $\lambda=450\text{nm}$, repetition rate 5MHz, average power 2-10 μW) to a 100 μm spot with an $f=5\text{cm}$ achromatic lens which also served as collection optics. The PL was collected with a fiber-coupled spectrometer (Ocean Optics USB2000).

An optical set-up was built where two identical optical paths were separated by a movable mirror. For experiments where the effect of the temperature or illumination were considered, a reference sample was placed in one of the arms under standard conditions and the other arm was used to probe the PL from a sample synthesized with temperature or under continuous illumination. In order to avoid inhomogeneities in the porous matrix fabrication that could affect the growth process, the two growth kinetics were performed on two pieces of the same sample which was halved right after the spin coating finished.

Results and Discussion:

In an initial set of measurements NC growth was carried out at room temperature contrary to previous reports where high (100°C) temperatures were used.²³ The time elapsed between the end of the spin-coating process and the initial PL measurements was always below 1 minute. PL spectra were collected by illuminating the sample during 300ms at different time intervals in order to map with enough precision the different stages of the growth process. Figure 1(d) shows a series of PL spectra attained at different times during nanocrystal growth (a selection of them is provided).

Figure 1. (a) XRD diffraction pattern of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ nanocrystals synthesized within a porous silica matrix. Dashed lines highlight diffraction peaks associated with crystalline $\text{CH}_3\text{NH}_3\text{PbBr}_3$. (b) Low and (c) high magnification TEM images showing the distribution of nanocrystals in the host and details of the lattice planes, respectively. Scale bars corresponds to 10 nm and 5 nm, respectively. (d) A series of photoluminescence (PL) spectra measured in situ at different times during the nanocrystal preparation procedure (from red to violet, 5, 30, 135, 150, 175, 250, 365, 460 and 825 s). Arrow indicates increasing times.

In order to perform an in-depth analysis of these data, PL spectra were fitted to a Gaussian function and the following magnitudes were extracted: PL intensity (I_{PL}), spectral position (λ_c) and full width at half maximum (FWHM). I_{PL} contains information on the amount of NCs and their crystalline quality, λ_c is dictated by the NC size and FWHM is related to the NC size distribution. Figure 2a-c shows the evolution of λ_c , I_{PL} and FWHM respectively as a function of time during a typical NC synthesis using a 20 wt.% concentrated precursor solution. λ_c presents a redshift characteristic of an increase in NC size. At the same time, I_{PL} undergoes a monotonic increase pointing to an improvement in NC photoluminescence quantum yield (PLQY), larger NC size and/or higher NC number. Finally, the FWHM undergoes a dramatic reduction going from 33 nm in the initial stages of the growth process ($\lambda_c=495\text{nm}$) to 23 nm at the end ($\lambda_c=525\text{nm}$). This latter reduction in spectral width is at odds with the expected trend for an increasing NC size and concomitant redshift and can thus be interpreted as a reduction in the PL inhomogeneous broadening associated with NC size dispersion. Then, as the NC synthesis proceeds within the nanoporous matrix, the mean NC diameter increases accompanied by a reduction in size dispersion or “focusing”.² Here it has to be noted that these FWHM values are

in line with those reported for state of the art $\text{CH}_3\text{NH}_3\text{PbBr}_3$ colloidal NCs¹⁰ and thus a small size dispersion is expected. Motivated by recent reports on the effect of illumination on the growth of the bulk material,²⁴ an identical sample was subjected to permanent irradiation throughout the entire growth process (see Section S1 in the SI). It was confirmed that constant light irradiation during NC growth leads to a slightly faster growth kinetics ending up in the same NC size at the cost of a poorer NC quality (Figure S1). Thus for the results of Figure 2, where irradiation time is two orders of magnitude below the constant illumination experiment, we expect a negligible effect of the probe light.

Figure 2. Time evolution of the (a) spectral position, (b) intensity and (c) FWHM of the PL maximum from a SiO₂ NP matrix infiltrated with a solution of 20 wt.% CH₃NH₃PbBr₃ precursors in DMF. Horizontal dashed line in (a) corresponds to the spectral position of bulk thin film emission. (d) Evolution of the NC radius as estimated from the spectral position of the PL (see section S2 in the SI) appear as grey dots and fittings to the Lifshitz-Slyozov-Wagner (LSW) model as black lines.

Next, the λ_c of the PL spectrum was translated into a NC radius r_{NC} (see details in Section S2 in the SI) to get an estimate of the modification in NC size during the growth process. A change from 1.2 nm in the initial stages of the growth process to 1.5 nm once it has finished was obtained (Figure 2d). In a first attempt to gain some understanding on the growth process, we fitted this time evolution to the Lifshitz-Slyozov-Wagner (LSW) model,^{25,26} which provides an analytical expression describing the growth kinetics of an ensemble of NCs in solution. Using the expression:

$$R = R_0 + k(t - t_0)^{1/n} \quad (1)$$

, where R (R_0) is the radius at time t (t_0), k is a temperature dependent reaction constant and n is a parameter indicating whether NC growth is being limited by crystallization reaction at the NC surface ($n=2$), diffusion of the precursors towards the NC surface ($n=3$) or re-dissolution of NCs with a size below a given critical radius ($n=4$). As fits of the NC radius evolution to a single value of n were unsuccessful, a more complex scenario than that of a single growth limiting factor is anticipated. For NCs synthesized under confinement in a porous matrix, the kinetics is strongly dependent on the diffusion coefficient (D) of the precursors, which itself depends on

solvent volume and precursor concentration. During the crystallization process, both solvent volume and precursor material are continuously decreasing due to evaporation and incorporation into NC respectively, albeit at different rates. This is in contrast to colloidal synthesis where the solvent volume remains constant and the precursors undergo a monotonical decrease as they are consumed through the NC growth. Hence we expect the D and k to change during the process, something that becomes evident upon a close look to the size evolution, where three different regions can be clearly observed, as shown in Figure 2(d).

As an initial fit of the experimental data to a single exponent in equation (1) did not yield satisfactory results, another attempt was performed employing genetic algorithms and leaving k and n as free parameters, imposing only that different growth regimes would follow the sequence $n=2,3,4$. The latter was based on the following discussion. Under confinement, the precursor is initially present in a solvent rich environment favoring its diffusion and evolves towards a system with shortage in diffusive material. We expect the solvent volume to decrease continuously via evaporation, while the precursor quantity is constantly decreasing as NCs grow. We therefore assume a continuous decrease in the diffusion coefficient, which justifies that in the early stages the growth kinetics are limited by the liquid-solid phase transition reaction ($k \cdot r \ll D$) (see Section S3 in the SI). In this scenario, $k=k_2$ remains constant, as its components are not changing (see equation S4). With increasing time, the diffusion coefficient decreases and the reaction becomes diffusion controlled ($k \cdot r \gg D$). In this regime, $k=k_3$ is expected to change with time as it depends directly on the diffusion constant. However, in order to be able to fit the data, we assume a constant average value for k_3 . Finally, for long times, the process is likely to become limited by the dissolution of smaller particles. Here again, $k=k_4$ is expected to change with time, but only an average value allows fitting. We note that the power law dependency is

only valid if the limit approximations are fulfilled. In the transition regions between the different limitation regimes, a pure power-law dependency is not applicable, explaining the discontinuities present in our fittings. Thus, while this fitting procedure is based on averaged parameters and cannot describe transitions between the different growth regimes, it clearly evidences a change with time of the growth limiting factor.

We have next considered the role of precursor concentration C_0 in the growth kinetics, since, as shown previously,²³ the NC size in the present synthesis can be controlled through $[C_0]$ in the solution spin casted on the porous matrix. Figure 3 displays results for samples grown using $[C_0] = 20, 5$ and 3 wt.% which leads to NC emitting in 524, 516 and 512 nm upon completion of the process. While the growth takes place on a similar time-scale as those discussed above, a zoom to the initial stages is presented to better appreciate the difference (data for the full process are shown in Figure S3). From Figure 3a it is evident that decreasing $[C_0]$ not only leads to a smaller NC size but also to a slower growth kinetics, as expected due to a reduced amount of precursors in the solution. Interestingly the evolution of the size dispersion of the NCs is also affected as evidenced by the results presented in Figure 3b. Here it is clear how the final FWHM increases as the precursor concentration decreases. Further, the time evolution of the FWHM also changes with precursor concentration. This can be clearly seen in Figure S4 where FWHM, related with size dispersion, is plotted against λ_c , given by the NC size. As $[C_0]$ is reduced the NC size dispersion goes from a focusing to a defocusing scenario. The above trends in the evolution of FWHM with precursor concentration are similar to the outcome of Monte-Carlo numerical simulations employed by Talapin and co-workers to reproduce the colloidal synthesis of NCs.²⁷ There, in the presence of large amounts of precursor a focusing of the NC ensemble size dispersion takes place in the initial stages of the process, where a population of small NCs is

present, followed by a defocusing once the precursor concentration drops below a certain threshold level $[C_{th}]$ and Ostwald ripening dominates NC growth. In our case, when using the highest precursor concentration (20 wt.%), after an initial growth in which the FWHM hardly changes, a strong focusing takes place reducing the FWHM from 32 to 24 nm. However, the precursor concentration never drops below $[C_{th}]$, for which NC dissolution starts and defocusing kicks in, likely due to the fact that NC growth takes place together with solvent evaporation. For the intermediate case (5 wt.%), precursor concentration is never large enough for the focusing process to complete and the NC growth stops in the initial stages of it. Finally, for the lowest $[C_0]$ (3 wt.%), the precursor concentration is initially below $[C_{th}]$ leading to a defocusing which stops once the concentration goes above the threshold level. Here the growth process is completed when the concentration is still low and defocusing has barely started.

Figure 3. Time evolution of the spectral position (a) and FWHM (b) of the PL peak from a SiO₂ NP matrix infiltrated with a solution CH₃NH₃PbBr₃ precursors in DMF having a concentration of 3% (orange dots), 5% (green dots) and 20 wt.% (red dots).

The role of temperature on the growth kinetics was also explored by simultaneously probing the emission from two halves of the same porous matrix infiltrated with a [C₀] = 20 wt.% solution and placed on the two arms of the optical set-up where one of them contained a hot plate at a fixed temperature. For the case of bulk LHP, temperature has been known as a key factor during the synthesis process to induce crystallization.²⁸ For the case of colloidal NCs, the two most widespread approaches, i.e., hot injection and ligand assisted re-precipitation, take place at elevated temperature or room temperature (RT), respectively.⁵ Several recent works have considered the role of temperature on different colloidal-based synthesis of LHP NCs. It was found that, while increasing T leads in general to a faster growth, the final NC size can be smaller^{9,14,15} or larger¹¹ than those grown at RT depending on whether fully inorganic or hybrid organic-inorganic NCs are grown. Here we have considered the growth for RT and 75°C in order to evaluate the role of this parameter. Figure 4a shows the time evolution of the PL peak position and Figure 4b its FWHM for the two temperatures under consideration. Here it is evident that increasing T lowers the growth rate and leads to a smaller final NC size, evidenced by a lower λ_c . Further, increasing T leads to a defocusing behavior with the FWHM undergoing a rapid increase from the initial stages of monitoring. Please note that rising T gives rise to two phenomena that have opposite effects on the growth rate. On the one hand, it causes diffusion to enhance, which should imply a higher growth rate. On the other, it induces a faster solvent evaporation, which hinders growth. Our observations indicate that the latter effect prevails over the former, leading to a scenario where monomer diffusion is drastically reduced by evaporation

so that growth and size focusing are quenched. Another interesting conclusion of this analysis is that limiting the synthesis volume by using of nano-reactors forces crystallization even at RT, for which an incomplete reaction is known to take place for the case of their bulk counterpart.

Figure 4. Temporal variation of (a) the spectral position and (b) the FWHM of the PL from a SiO_2 matrix infiltrated with a 20 wt.% $\text{CH}_3\text{NH}_3\text{PbBr}_3$ precursors solution and left at room temperature (grey dots) and 75°C (black dots).

Finally, based on our observations, we propose a growth mechanism for LHP NCs in metal-oxide mesoporous matrices. Upon depositing the precursor solution on the mesoporous matrix, nucleation takes place already during the spin coating process. This nucleation stage is much faster than we can resolve in our experiment (5 seconds). A change in color, from the transparent appearance of the matrix infiltrated with the precursor solution to the greenish characteristic of

the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ NC- SiO_2 system, is already observed in the infiltrated porous matrix after the spin coater is stopped. Following this initial stage, NC growth takes place within the pores of the matrix containing remains of the initial amount of solvent. Here a complex scenario takes place where precursor concentration varies according to NC growth (deploys precursor concentration as it is incorporated into the NC surface) and solvent evaporation (increasing precursor concentration). The effect of the different parameters under consideration on the observed kinetics will depend on the way they affect these two processes. In this sense, a number of guidelines can be provided in order to optimize NC growth in this type of matrices. Regarding concentration, which has shown to be an effective way to tune the NC size, if one wants to maintain the ensemble size dispersion, a better approach can be the use of smaller pore size in the matrix,²⁰ as changing the pore size has been shown to be an effective way to control the NC size.¹⁶ Further, for a given pore size, high precursor concentrations will lead to lower size dispersions although a compromise will have to be found in order not to introduce an overlayer of bulk material.^{20,23} As far as the reaction temperature is concerned, contrary to the bulk synthesis, RT conditions will provide the appropriate balance between growth dynamics and evaporation rate to yield high quality larger NCs. While the present study is restricted to the growth of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ NCs, a similar mechanism is expected for other material compositions and solvents albeit, due to different solubility or lead-to halide affinity, the dynamics could vary. Finally it should be mentioned that, though out of the scope of the present work, a relevant factor to be considered in the future is the role of the surrounding atmosphere. For the case of LHP in the shape of thin films, the role of the atmosphere during material fabrication on film morphology and optoelectronic properties has been studied over the past years.²⁹⁻³¹ For the case of LHP NCs growth within nanoreactors the surrounding atmosphere will certainly play a

relevant role not only on the formation of the material itself but also on the modification of the metal-oxide scaffold.

Conclusions

In summary, we have presented a detailed study of the way LHP NC growth takes place within porous matrices depending on different external factors such as light illumination, precursor concentration or reaction temperature. This fabrication method, closer in nature to those commonly used to obtain LHP thin films, allows the preparation of ligand-free high quality NCs with improved chemical and photo-stability and has demonstrated potential for device fabrication. While a particular study will probably be needed for porous matrices of different nature, the present study already provides valuable guidelines to attain homogeneous ensembles of NCs with controlled size.

Supporting Information.

The following files are available free of charge.

NC growth under irradiation; NC radius determination; L-S-W model; Evolution of FWHM and λ_c for different precursor concentration. (PDF)

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