Emergence of lead halide perovskite colloidal dispersions through aggregation and fragmentation: insights from the nanoscale to the mesoscale†

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The structural and optoelectronic properties of mixed halide perovskite colloidal precursor dispersions are investigated. With increasing concentration, we observe four stages of growing structures, which affect the thin film morphology: (I) nanoparticles, (II) increasing size of nanoparticles, (III) formation of large aggregates/complex clusters and (IV) fragmentation of large aggregates.

Hybrid organic lead halide perovskites are an exciting class of materials. Apart from their stellar optoelectronic properties which enable various photovoltaic and optoelectronic applications, the ease of tunability of chemical compositions and structural identities have enabled efforts in structuring the material in its various states of assembly. The entire range of solution-processed structures, extending from nanocrystals, to thin films and to single crystals share similar colloidal origins1–3 of their respective precursors. This seemingly innocuous property of the precursors imparts intensive degrees of freedom to the fluid sol state. Moreover, the precursors are known to be dynamic and strongly affected by processing parameters and in turn impact the resulting thin film morphologies.6 The colloidal nature itself emerges due to the non-trivial, physico-chemical interactions7 between the dispersed solid precursors and the solvent media. Despite the existing knowledge about mechanisms of nucleation and growth of nanoparticles,8 it remains imperative to understand the structure of the colloids in the fluid phase, in order to obtain predictive correlation between initial precursor chemistry and the final thin film morphology of hybrid perovskites.

Results

Foremost, the optical properties of precursor sols are studied by UV-vis measurements. A series of concentrations for the precursors are utilized in order to decohere the effects and mark the boundaries of changes within colloid structure by the aggregation and fracture of entities within the fluid phase. A stock solution of an exemplary concentration has been prepared and is then sequentially diluted in order to obtain lower concentrations of interest. The samples are measured against a blank of the solvent mixture of 4 : 1 of (dimethylformamide) DMF : (dimethyl sulphoxide) DMSO, in which the precursors have been dispersed.

The first sol investigated is a dispersion of the precursors of CH$_3$NH$_3$PbBr$_3$ (CH$_3$NH$_3$Br + PbBr$_2$ in 4 : 1 :: DMF : DMSO) for which a stock solution of 3 M was prepared. The absorbance properties of the 3 M and subsequent lower concentration precursors are measured sequentially, in order to regulate similar physical and atmospheric conditions (Fig. 1a). The data suggest the presence of two distinct (and three identifiable) structural regimes (Fig. 1b). For precursors of high concentrations ranging from 3 M to around 1.3 M, the dispersions all display similar absorbance profiles with absorption onsets around 405 nm. The absorption onsets of precursors of concentrations in this high concentration regime (Fig. 1b; III), appear slightly red-shifted with each dilution (Fig. S1†). From 1.3 M until 0.45 M (regime II), the precursors express stabilized structural sizes wherein the absorbance characteristics remain predominantly invariant with decreasing concentration, displaying minor blue shifts with subsequent dilutions. At concentrations below 0.45 M (regime III), the precursor sols show noteworthy blue-shifts in their absorption onsets with each dilution. Individual material absorbance peaks could not be resolved due to saturation at the detector at absorbance values around 2.5 wherein the maximum of the absorbance signal is lost due to its high magnitude, owing to the high absorption coefficient of the precursor. For a singular concentration of 2.8 mM, the absorbance maxima could be resolved by the...
detector, and a quasi-Gaussian profile of the absorbance peak is obtained.

Thereafter, the size distribution of particles in the precursor fluid is probed through dynamic light scattering (DLS) measurements for MAPbBr₃ at concentrations ranging from 3 M down to 0.1 M. The auto-correlation function exhibited two distinct decay timescales suggesting two discernible structure distributions of scattering objects (Fig. S3†). The first decay corresponds to hydrodynamic radii of structures within the nm range (Fig. 1c) and the second decay exhibits hydrodynamic radii of structures within the µm range (Fig. 1d). Both structures have an exponential growth of representative entities with increasing concentration.⁹

For the precursors corresponding to MAPbI₃, a stock solution of 1 M has been prepared. A higher concentration is not intended for the stock solution since the fluid precursor quickly turned translucent due to high supersaturation and the growth of large clusters threatened the integrity of measurements. The absorbance data is non-trivial and what at first glance appears as measurement artefacts are in fact, rich optical signatures from plumbo-iodate complexes (Fig. 2a), as confirmed by multiple sets of measurements. Individual absorbance signals are isolated from PbI₂ at around 340 nm; for [PbI₄]²⁻ at 438 nm; for [PbI₃]⁻ at 480 nm and for [PbI₂][I] as well as [PbI₃][I] at more red shifted wavelengths. For [PbI₃][I], the absorption edge varied strongly with concentration. For [PbI₄][I], the absorption edge is not visualized. It is striking to observe the identical signatures from the plumbo-iodate complexes within the precursor corresponding to MAPbI₁.₅₀Br₁.₅₀ at the exact wavelengths as designated for the complexes obtained from the MAPbI₃ precursor (Fig. 2c). Moreover, at concentrations beyond 1 M, the absorbance data of MAPbI₁.₅₀Br₁.₅₀ provides a rare and fascinating insight into the structure evolution of the concentrated fluid phase. It is observed that within the high concentration regime, the absorbance signal corresponding to [PbI₄][I] starts diminishing with increasing concentration and the absorption onsets experiences a blue shift until 3 M (Fig. S2†).

Within DLS, unlike the case of MAPbBr₃ where 2 distinct decays were isolated and fitted to nanoparticles and larger clusters, in the case of both, MAPbI₃ and MAPbI₁.₅₀Br₁.₅₀, no clear distinctions for different structural size distributions could be made (Fig. S3†). The DLS data corresponding to MAPbI₁.₅₀Br₁.₅₀ (Fig. 2d) indicate hydrodynamic radii within the µm range, which show an exponential increase with increased concentration. The DLS data for MAPbI₃ (Fig. 2b) suggest the presence of smaller scattering objects which is however not indicative of the true nature of the fluid precursor. This is evident from the raw scattering intensities of the different precursors: I[MAPbI₃] > I[MAPbI₁.₅₀Br₁.₅₀] > I[MAPbBr₃] (Table S1†).

Materials and methods

Precursor dispersions were prepared by initially combining the inorganic components of PbBr₂ (Alfa Aesar, 98%), PbI₂ (Sigma-Aldrich Inc., 99%) in a 4:1:v:v mixture of anhydrous N-N-DMF (Sigma Aldrich, >99.8%) and anhydrous DMSO (Sigma Aldrich, >99.9%). To this stock solution, the organic components of CH₃NH₃I (Solaronix) and CH₃NH₃Br (Dyesol) were added and the dispersions were mixed and sonicated in order to dissolve the precursors in clean vials. All preparations were carried out with chemicals as provided by the manufacturer in a nitrogen filled glove box atmosphere.

UV-vis spectroscopy was carried out with a PerkinElmer Lambda 35 spectrometer in a wavelength range from 300 nm to 700 nm utilizing a halogen and a deuterium lamp.

Fig. 1 (a) Absorbance data of MAPbBr₃ precursor at designated concentration as indicated, (b) correlation between precursor concentration and absorption onset wavelength [black], photon energy [red], evolution of hydrodynamic radii of (c) nanoparticles and of (d) colloidal clusters within precursor.

Fig. 2 Absorbance data corresponding to the precursor of (a) MAPbI₃ and (c) MAPbI₁.₅₀Br₁.₅₀ and the corresponding average particle size distribution obtained from DLS measurements as a function of concentration of the said precursors (b) MAPbI₃ and (d) MAPbI₁.₅₀Br₁.₅₀.
Dynamic light scattering (DLS) measurements were conducted with a 3D LS Spectrometer from LS instruments with controllable laser power with a maximum power of 21 mW HeNe laser (632.8 nm). Scattered intensity from the samples were collected at right angles from the laser source. The distribution of relaxation times (τ) was then obtained from the autocorrelation functions by means of an inverted Laplace transformation of the said function through a regularized positive exponential sum (REPES) routine. A stretched exponential was used to fit the correlation decay profiles for the dispersions and the average decay time was calculated with a weighted mean of the correlation functions. Hydrodynamic radii were calculated from the DLS data based on the refractive index of the individual solvents and solvent mixtures (Table S2†).

Thin films were prepared by the one-step, antisolvent assisted route† and annealed at 100 °C, within a nitrogen glovebox.

Grazing incidence wide angle X-ray scattering (GIWAXS) measurements on thin films were carried out under vacuum conditions on the Ganesha 300XL SAXS-WAXS system with an operating wavelength of 1.5406 Å. An incidence angle of 0.1° was employed. GIWAXS data was recorded on a Pilatus 300k area detector at a sample-detector distance of 100 mm. GIXSGUI† was used for necessary data corrections and analysis.

**Discussions**

Colloidal precursors are complex species and as evident, are strongly affected by the chemical environment. Fig. 3 describes the fate of the colloidal dispersion as a function of increasing concentration of the precursor in the solvent media. At low volume fractions, the dispersed particles are small (nanoparticles) and experience quantum confinement effects. This behaviour is reflected through the red shifts within absorption profiles of growing structural entities as the concentration of the solute is increased within the dispersion. An increase in volume fraction favours the growth of small entities into larger clusters, rather than increased number of smaller individual particles. As a result, higher order complexes (more relevant for I-containing precursors) or simply particles with increased size/increased co-ordination emerge with increasing concentration. At any given volume fraction, the size/structure of the dispersed phase/solvent complex is limited by the concentration of the precursor. In this regime, growth/structural evolution of nanoparticles is favoured as the dispersed entities have high degree of translational freedom which affords a larger volume available to the said entities for diffusion (entropy favours growth). The above growth processes fall under phase I and II of the schematic in Fig. 3. These phases also coincide with the quantum size regime observed in the UV-vis measurements and serve as the explanation as to the emergence of new spectroscopic signatures from higher order Pb-X complexes with increasing concentration. Growth of nanoparticles continues until a stable cluster size is obtained by the dispersed phase. This phase lasts within a concentration range wherein the size of the colloids remains primarily unchanged but the dispersion experiences an increase in packing density. Once a critical packing density is reached (which varies with chemical composition, owing to changing interactions of the dispersed chemical species with the dispersion medium), any further increase in the concentration of the dispersed phase leads to the jamming of the colloid (phase III) as the volume available to clusters for diffusion (excluded volume) is depleted. Further growth of particle size is no longer favoured due to increased repulsion between the densely packed colloid clusters as the system enters a non-ergodic regime and the increased volume fraction of the precursors leads to a significant, nonlinear increase in the viscosity of the fluid marking a change in the rheology of the precursor (Fig. S4†). The diffusion of the particles is arrested and the viscosity induced shear forces in addition to the steric frustrations experienced by the colloidal clusters lead to the fragmentation (or deaggregation) of the erstwhile stable, homeomorphic particles to form smaller, more numerous and dissimilar clusters (phase IV). This explains the blue shift of the absorption tails at high concentration. Moreover, it is the same phenomenon responsible for MAPbI$_3$-Br$_{0.50}$ exhibiting drastically diminished spectroscopic signatures from the [PbX$_6$]$^{4-}$ complex, the largest of the various complexes expressed, within concentration regimes well within the supersaturation of the fluid phase.

The boundaries between different growth regimes in different dispersions are variable and the sizes of particles at specific volume fractions are strongly sensitive to the distinct chemical environment and the physical characteristics of the liquid media. Consequently, they cannot be directly compared.

It is worthwhile to note that the scattering intensity within DLS scales as $r^6$ with the particle radius (r). Thus, a particle 10 times the radius of another would scatter $10^6$ stronger than the other. A distinct decay corresponding to small nanoparticles, as was the case for MAPbBr$_3$ would be indicative of a
significant population of the colloidal precursors exhibiting the size within the nm regime, in order for the decay to even be sensitive to the measurement itself. This confirms the presence of distinctly polydisperse scattering objects as per DLS measurements.

Hydrodynamic radii obtained from the measurements overestimate the radius of the scattering particles. Moreover, for MAPbBr₃, each dilution leads to an increase in the excluded volume of the colloidal dispersion, providing the particles with an increased volume for diffusion. In the jammed state of the precursor, due to considerably increased viscosity, the packed clusters, in spite of a stabilized size, appear rather as a large scattering entity with slow diffusion timescales, which explains why the data affords extremely large hydrodynamic radii for MAPbBr₃. For the I-bearing counterparts, due to the presence of a plethora of solvent complexes of distinct sizes and shapes, the polydispersity is manifold and more complex as compared to the relatively simple Br-bearing precursor. The DLS measurements for the MAPbI₃ dispersion is challenging to probe and the data and the trends are not truly representative, possibly due to Mie scattering from the large solvent complexes, which would require angle resolved DLS measurements to account for the anisotropic scattering.

Perovskite precursors consist of structures possessing high flexibility. As a result, thin film morphologies are strongly affected by the rheology of the viscoelastic precursor sols. At nominal concentrations of the fluid precursor, crystallization is guided through thermodynamically controlled routes and thin films form such that the system settles into the minimal energy state, with high degree of morphological order (Fig. 4a) and a state of minimum energy is attained by the emergence of {100} facets with a narrow azimuthal spread. At higher concentrations, the viscosity of the precursors sees an increase as dispersed particles obtain jammed characteristics while existing under entropic stress. The high volume fraction of the dispersed precursors drives the fluid well into supersaturation and resultant thin films are formed by kinetic arrest of the precursor, as crystal growth occurs through stochastic routes, far-off from thermodynamic equilibrium. Thin films formed from such precursors exhibit reduced microstructural homogeneity, as kinetically guided crystallographic directions emerge {111} with broad azimuthal spreads (Fig. 4c).

Conclusions and outlook

The structural and optoelectronic properties of mixed halide perovskites colloidal precursor dispersions are investigated in order to improve the understanding of the chemical and physical nature of perovskite sols. The study is of relevance since in many cases the formation of thin perovskite films is based on solution-processing using precursors, being prepared under representative conditions as those utilized within the present study. Prevalent protocols utilize chemical tailoring of precursors, which are demonstrated to possess polydisperse structural species of varying chemical compositions. The study probes the growth of chemical entities in dispersions and identifies the emergence of different structural complexes and their evolution from nanocrystals to growing complex aggregates. The study suggests that mixed halide perovskites colloidal dispersions bear precursors of their individual parent precursors. Thin films based on colloidal precursors grow at the expense of the very structural entities present within these dispersions. Structural inhomogeneities have been linked to variations in photovoltaic performances²² and bear direct relevance in the case of functional devices. The origin of structural and possibly chemical heterogeneities within thin films may very well be correlated to the structures prevalent within the dynamic fluid phase and underlines the need for a better understanding of the non-trivial perovskite precursors.

Conflicts of interest

There are no conflicts to declare.

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References


