Unraveling Antisolvent Dripping Delay Effect on Stranski Krastanov Growth of CH$_3$NH$_3$PbBr$_3$ Thin Films: A Facile Route for Preparing Textured Morphology with Improved Optoelectronic Properties

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Inorganic-organic hybrid perovskite materials have been a topic of interest for last few years due to their superior optoelectronic properties. However optical properties of perovskite materials are strongly dependent on the film morphology. Textured film morphology is expected to have higher light absorption as well as light out-coupling efficiency compared to smooth film. There have been numerous methods for controlling and optimizing film morphology to achieve high efficiency in solar cells and light emitting diodes. Here we have demonstrated that controlled anti-solvent treatment at low temperature can give Stranski-Krastanov growth in CH$_3$NH$_3$PbBr$_3$ thin films with superior optical and electronic properties for light emitting diode application. We have studied their photoluminescence properties at micro- to nano scale by fluorescence microscopy, hyper-spectral imaging and scanning near-field optical microscopy. We have demonstrated that the nanostructured micro-islands are highly emissive because of large quasi Fermi level splitting (QFLS) due to the localization of free charges in the smaller crystals. We have shown that the photoluminescence as well as electroluminescence can be improved by at least seven-fold due to the presence of micro-island on a smooth background film enhancing light out-coupling. Photo-induced photoluminescence enhancement is also observed in smooth film while micro-islands show photo-degradation.

Keywords: Stranski-Krastanov growth, fluorescence microscopy, hyper-spectral imaging, scanning near-field optical microscopy, nanostructured micro-islands, quasi Fermi level splitting

Introduction

Halide based perovskite light emitting diodes (PeLEDs) have become efficient and fastest-improving LED technology to date, as external quantum efficiencies (EQE) of perovskite-based light-emitting diodes have exceeded 20% in just a few years of research. The main reason behind the success of perovskite-based LEDs is that the thin films of these materials can be present with high defect tolerance, large carrier diffusion lengths, high photoluminescence quantum yield, ambipolar charge transport, wide-range emission tunability, and high colour purity. These properties make the perovskite LEDs promising candidates for display and solid-state lighting applications. However, perovskites grains show heterogeneity in their optoelectronic properties regardless of their synthesis process, heterogeneity in their optical properties is present even in thermally deposited films. Most of the studies have discovered that the PL heterogeneity is indicative of variations in the local density of non-radiative decay channels. Smaller grains increase the radiative recombination fraction due to increased carrier concentration while in larger crystals carrier may diffuse further due to large diffusion length. Therefore, bimolecular radiative recombination fraction increases in large crystals. The presence of non-radiative pathways in perovskite nanocrystals strongly depends on the processing conditions as well as the film morphology. Apart from the high PL quantum yield high light out-coupling is another parameter to achieve high efficiency in perovskite LEDs, therefore textured morphology is preferable over smooth film. Recently Qin, Jiajun, et al. had also demonstrated that mixed crystal size can be better than uniform smooth film. Controlled crystallization of perovskite materials reported by various research groups include gas-assisted crystallization (GAC), using different co-solvents to retard the rapid reaction between perovskite precursors, substrates pre-heating and anti-solvent treatment. The anti-solvent treatment has been proved to be a very efficient method for controlling the growth of perovskite crystals. In this article we have demonstrated that the controlled anti-solvent treatment can result in either Frank–van...
der Merwe like (layer-by-layer) growth or Stranski-Krastanov (layer-plus-island) growth in methyl ammonium lead tribromide (CH$_3$NH$_3$PbBr$_3$) thin film. Textured perovskite films show the homogeneously scattered micro meter sized islands structures consisting of 20–40 nm CH$_3$NH$_3$PbBr$_3$ crystals, these micrometre sized areas are referred as micro-islands (MIs). Steady state or time resolve PL measurement of these MIs reveal the overall PL enhancement due to increased PL lifetime. However, to understand the origin of low or heterogeneous PL in these perovskite thin films, we need to investigate PL at various length-scale. There are various techniques including super-resolution microscopy, fluorescence microscopy, hyper-spectral imaging and scanning near-field optical microscopy (SNOM) to study PL heterogeneity at micro to nano scales. These types of microstructures are also known to have better light out-coupling efficiency in PeLEDs. We studied these MIs using fluorescence microscopy, hyper-spectral imaging and SNOM to investigate the origin of high PL in micro-islands and PL quenching in smooth perovskite thin films.

Results and discussion:

Morphology optimization
Perovskite thin film morphology can be well understood by studying nucleation and growth mechanism. In this work, we have used anti-solvent treatment to prepare CH$_3$NH$_3$PbBr$_3$ perovskite thin films as shown in Fig. 1a. Depending on the adsorption thermodynamics and the kinetics of crystal growth the prepared film can take any of three forms namely (i) Volmer-Weber (island), (ii) Frank-van der Merwe (layer by layer) and (iii) Stranski-Krastanov (layer plus island) (see Fig. 1b-d).

The film prepared without any anti-solvent treatment results in large cube-like crystals with less than 50% film coverage, we will refer this film as controlled film. Slow drying of precursor solvent during spin coating leads to heterogeneous nucleation followed by slow Volmer-Weber (VW) growth (Fig. 1b) which can give large cube like structure due to strong adatom-adatom interaction with the nucleation sites compared to the weak interaction between adatom-substrate surface. Frank-van der Merwe (FM) growth has the opposite characteristics to that of VW growth where adatom-adatom interaction is weaker than

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**Fig 1** Scheme for preparation of perovskite film with controlled morphology. Scale bar in SEM image of anti-solvent treated and without anti-solvent treated film, (b) schematic of Volmer-Weber (island formation), (c) schematic of Frank-van der Merwe (layer-by-layer) and (d) schematic of Stranski-Krastanov (layer-plus-island) growth.
Adatom-substrate interaction leading to more uniform and homogeneous nucleation. To prepare uniform film homogeneous nucleation is necessary; this can also be achieved by fast nucleation followed by slow growth process.\(^{31}\) One of the common approaches to achieve fast nucleation is anti-solvent treatment.\(^{42}\) In this case anti-solvents are non-polar (or less polar than the precursor solvent), miscible with solvent but immiscible with perovskite precursor. Adding anti-solvent during spin coating can result in supersaturation and therefore fast nucleation is achieved. This can trigger homogeneous nucleation leading to smooth uniform film. We have optimized the perovskite morphology by controlling the delay time for anti-solvent treatment as shown in Fig. 2. It should be noted that there are two types of film formation during anti-solvent treatment; (i) Frank–van der Merwe (layer-by-layer) and (ii) Stran-ki-Krastanov (layer-plus-island) depending on the anti-solvent dripping delay time. Stran-ki-Krastanov (SK) growth is normally seen in epitaxially grown film on a smooth surface. SK can also be realized as the intermediate growth model of 2-dimensional layer (Frank-van der Merwe) followed by 3-dimensional island (Volmer-Weber) formation. There have been several theoretical as well as experimental studies to understand SK growth in inorganic thin films.\(^{45,46}\) Song et. al. had also shown that SK growth is present at the initial stage of moisture condensation\(^{47}\) but SK growth in solution processed perovskite thin film is sparse.\(^{48}\) General belief is that the two competing factors, energy and entropy play a crucial role in SK growth. Therefore, controlling anti-solvent dripping delay time can control the entropy, therefore energetically unstable film leads to 2-D layer to 3-D island formation. It is shown in Fig. 2e that the formation of micro-islands (MIs) can be realized if we drip the anti-solvent at 30th–40th second from the start of spin coating (3000 rpm for 80 seconds). If the dripping delay time is 10th–20th sec the film becomes more uniform and smoother. However, if the anti-solvent dripping delay is more than 50th second from the start of the spin coating, these MIs start to disappear again. A better understanding of crystallization based on time varied anti-solvent treatment in our case can be understood in terms of change in chemical potential of nucleation site (\(\mu_{ns}\)) as spin coating proceeds. VW growth is characterized by negative slope of \(\mu_{ns}\) which indicates strong adatom–adatom interaction, whereas positive differential of \(\mu\) implies strong adatom–surface interaction, and it is responsible for FM growth mode as shown in Fig. 3a. Therefore, SK growth can be seen as a positive derivative of \(\mu_{ns}\) curve followed by a negative differential of \(\mu\) afterward. Variation of Gibbs free energy predicts a critical radius, which has to be reached before crystallization to start (Fig. 3c).\(^{43}\) Variation of Gibbs free energy can be given as\(^{43}\)

Fig. 2 Optimization of perovskite film for improved light out-coupling and high extraction efficiency design by spin coating. FESEM image of (a) controlled film showing the presence of ~10 µm sized micro-cubes with a partial film coverage (b–f) perovskite films obtained by anti-solvent treatment using chlorobenzene as an anti-solvent and benzylamine as an additive to the chlorobenzene. Anti-solvent treatment of these films was performed by optimizing the delay time for the treatment in an 80-second spinning program. Films shown in (b) – (f) are treated at 10, 20, 30, 40 and 50 seconds after the start of spinning respectively.
\[ \Delta G = \Delta G_s + \Delta G_V = 4\pi r^2 \gamma + \frac{2}{3} \pi r^3 \Delta G_V \]

where \( r \) is the radius of the simulated spherical particles (nucleus) and \( \gamma \) is the interfacial energy or surface energy between the supersaturated solution and crystalline surface and \( \Delta G_v \) is bulk free energy per unit volume. Maximization of Gibbs free energy can be seen as a point of phase transition from liquid to crystal and corresponds to equalization of chemical potentials of liquid and nucleation site. In Fig. 3a \( n_0 \) represents the critical number of particles to be added to nucleation site in order to form a stable nucleus. Once nucleus becomes stable volume term in Gibbs free energy dominates and lowers the Gibbs free energy of the nucleation site therefore resulting in a negative slope in \( \mu - n \) graph (Fig. 3d), since negative slope in \( \mu - n \) is responsible for VW growth and this explains the formation of scattered micrometre sized crystals with less than 50% coverage in controlled film. This indicates that the natural tendency in spin coating is to proceed through VW growth unless the variation in \( \mu_{ns} \) is controlled by external trigger such as by controlling pressure, temperature or the solution concentration. Fig. 3d shows the variation of chemical potential as spin coating proceeds. In our case we have chosen 80 seconds of spinning program (3000 R.P.M.), If we assume that the critical radius is reached around 20-25th second (film colour changes) we can explain the observed morphologies. As anti-solvent dripping can increase the chemical potential of the system by effectively increasing the concentration of the solution by extracting excess solvent. If we drip the anti-solvent at 10th second after spinning starts, since the Gibbs free energy

![Schematic diagram of controlling chemical potential with the help of anti-solvent treatment during crystallization of perovskite films.](image)

(a) change in chemical potential as a function of adsorbed particles/molecules (b) change in chemical potential from liquid phase to crystalline phase (c) variation of Gibbs free energy as a function of particle radius and (d) proposed variation of chemical potential during the antisolvent dripping. Dotted line represents chemical energy variation without anti-solvent dripping while solid lines represent chemical energy variation at different antisolvent dripping delay time.
has not reached its maxima therefore part of increase in Gibbs free energy by anti-solvent treatment is utilized to raise G to its maxima therefore effective positive change in µ is little in this case (which corresponds to FM growth which very is weak for this films). After few seconds of antisolvent treatment concentration of the solvent stabilizes and crystallization occurs through VW growth and we obtain full coverage film but with a little higher roughness and bigger crystal size with respect to other antisolvent treated films (Fig. 2b and Fig. 4a). If antisolvent treatment is done at 20th second which is very close to crystallization point, a very high slope in µ-n graph results in FM growth much effectively and even after few seconds when concentration stabilizes the chemical potential of nucleation site remains higher compared to substrate chemical potential for few seconds and crystallization keeps proceeding through FM growth and spends much longer time in FM growth mode, and therefore results in smoothest films (Fig. 2c, Fig. 4b). Whereas if anti-solvent treatment is performed at 30 or 40th second of spinning, change in concentration forces the crystallization to FM mode for few seconds (until concentration of solvent stabilizes) but it returns to VW mode faster compared to films treated at 20th second. Therefore crystallization proceeds through a combination of FM and VW growth mode which is SK mode and consequently we achieve formation of islands in case of anti-solvent treatment at 30 – 40 seconds (Fig. 2 d,e and Fig. 4c,d). If we wait up to 50 seconds for anti-solvent treatment since crystallization has occurred through VW mode from 20-50 seconds this time we don’t have a flat substrate to form smooth film, but as soon as we add anti-solvent growth mode changes from VW mode to FM mode and we achieve full coverage film but when it comes back to the VW mode, there is not much of time left for film to proceed through VW mode and form islands. rms roughness of films prepared at 30 seconds of delay time and 50 seconds of delay time are almost same but morphologies of two films are different which indicates that film treated at 30 second delay time spends more time in VW mode after antisolvent treatment whereas film treated at 50 second spends more time in VW mode before antisolvent treatment. Therefore, we conclude that the smoothest films in anti-solvent treatment can be achieved if we drip the anti-solvent exactly at the point of formation of stable nucleus. And we can design micro-islands if we drip the anti-solvent at a suitable time when both FM and VW growth modes contribute equally resulting in a SK growth. The rms roughness of these film is shown in Fig. 4f. For more quantitative analysis further experiment/simulation/modelling is needed to understand SK growth in perovskite thin film. In this study we call these SK growth films as textured films because these films present the formation of micrometre-sized islands. These islands comprise of smaller particle size (~ 20-40 nm) distribution (see Supplementary Fig. S1) compared to a relatively larger grain size (~ 300 nm) at the background. The XRD pattern indexes matches well to cubic MAPbBr3 for both the controlled and anti-solvent treated films (Supplementary Fig. S2). With the help of scanning electron microscope (SEM) and atomic force microscope (AFM) image analysis of MIs, the average height of MIs is found to be ~120 nm and an average distance of two such micro-island is around 3 μm (Supplementary Fig. S4), a 25x25 µm² area was

![Fig. 4 Perovskite film morphology optimization by controlling antisolvent treatment delay time.](image)

Fig. 4 Perovskite film morphology optimization by controlling antisolvent treatment delay time. Fig. a,b,c,d show AFM images of perovskite films treated at 10, 20, 30, 40 and 50 second delayed treatment. Fig. c shows variation of rms. film roughness vs antisolvent treatment delay which indicates that smoothest films can be achieved if treatment is done around 20th second after spinning starts, whereas textured film can be achieved only if treatment is done around 40 second delay.
scanned with the help of AFM setup for this measurement. The scan area is large enough to include a number of micro-islands in order to calculate the average height of these micro-islands.

**Photoluminescence measurement**

**Fluorescence imaging**

Controlled film shows very weak PL intensity so as the smooth perovskite film prepared by anti-solvent treatment after 10th – 20th second delay. This could be due to high PL quenching at the defect sites or at the hole transporting layer. The PL intensity was found to be maximized for the textured film prepared at 40th second delay amongst all the film types, though it was spatially inhomogeneous because of the presence of MIs. Film prepared at 30th second and 50th second delay show moderate PL intensity (Supplementary Fig. S5). The areas of the textured film that are away from the MIs are similar to the smooth film. Therefore, our main focus is to understand the spatially heterogeneous PL emission of the textured film. High PL intensity is the signature of low defect density and purity of the material. In fluorescence microscopy, we have observed that the PL intensity at MIs is much higher than that of the regions away from the islands (Fig. 5a), this could be obvious because of the anti-correlation of PL intensity and grain size. Fig. 5b is the overlay image of transmission and fluorescence mode image which indicates that the brighter regions are MIs. We speculate that the presence of MIs can improve the light out-coupling efficiency by providing the convex-concave geometry at the perovskite air interface, and thus it could help to improve the PL emission at least 7-fold in our case. SEM and AFM images of these MIs show the formation of a textured surface which can improve the light out-coupling efficiency. In Fig. 5c we show the histogram of PL intensity (arbitrary unit) to compare the contribution of dark and bright regions. Supplementary Fig. S6 depicts that the PL intensity counts < 90 grayscale value (GSV) are from the regions which are away from the MIs whereas 100 GSV mark the boundary of the MIs. Therefore, we have divided the histogram into three different regions; the low-intensity region shows the PL intensity clustered around 20 GSV whereas high-intensity end shows a peak around 140 GSV. This indicates that the MIs can increase the PL intensity at least 7 times compared to the smooth films (non-island site is itself a smooth film). Inset of Fig. 5c is just the magnification of the y-axis for the high-intensity region. Fig. 5d shows a good linear correlation coefficient (R = 0.72) between PL intensity and the area of MIs. Although the high-intensity regions are associated with the larger MIs, this relation seems to saturate around a characteristic micro-island area 1.8 µm². Next, we performed the steady-state PL measurement for all the samples (see supplementary Fig. S5), by taking the ratio of integrated PL intensity, we observed that the PL intensity from textured films show ~10-fold increase from controlled film PL intensity and ~7.5-fold increase from smooth films, which is consistent with the observations from the fluorescence microscopy. With the help of AFM image analysis and cross-sectional FESEM image (Supplementary Fig. S4) we have found that the local volume fraction increased at MIs sites is only ~32% whereas overall volume fraction increased is ~6.8%. This analysis indicates that the 750% increase in PL is not just the consequence of higher

![Fig. 5](image-url)
effective film thickness but it could be the result of high PL quantum yield due to the smaller crystal size. Improved photon absorption by light trapping as well as PL out-coupling due to MIs sites. Recently, we have also shown that this type of textured morphology forms a better perovskite/HTL interface in a N-I-P structured PLEDs. We believe that the inhomogeneity in the widefield PL mapping is mainly because of the charge carrier confinement as well as trap distribution since the contribution of diffusion-limited decay pathways is weak for widefield illumination.

**Hyper-spectral PL imaging**

To investigate detailed photoluminescence properties of these MIs we have carried out hyperspectral PL imaging on these MIs as well as smooth background film. The PL mapping by hyperspectral imaging is still diffraction limited; therefore, the limitation due to grain boundaries could not be resolved in smooth film. To find out the mechanism of non-radiative recombination losses in smooth perovskite films, scanning near field optical microscope (SNOM) is introduced to investigate such lateral PL intensity variations. From hyperspectral PL microscopy, we can see that there are regions of the textured film at which the PL spectrum is more skewed; these are the areas of low PL intensity. The shape of the spectrum is fitted with a bi-Gaussian function (Fig. 6, S7). We attribute these two Gaussians as a result of two different emitters; the presence of two emitters could be related to the different size of the crystals. Some of the high energy photon can be reabsorbed at low energy sites. Thus, the PL intensity depends on the fact that how efficiently the charge carriers can diffuse toward the quencher sites and also on the quenching efficiency of the quencher. PL inhomogeneity in the micro-cube for the controlled film can be found in supplementary information (Supplementary Fig. S8). To investigate further, we have estimated quasi Fermi level splitting (QFLS) at the micro-island site as well as for the background film (Supplementary Fig. S9). QFLS is the characteristic of purity of the material and normally indicative of maximum achievable open-circuit voltage in perovskite solar cells. Here we have calculated QFLS for the brightest, moderately bright and least bright location of the film using generalized Planck’s law.

\[
\ln \left( \frac{\mathcal{Y}_{PL}(E)}{10^{23}E^2} \right) = \frac{\Delta \phi}{kT} - \frac{E}{kT}
\]

Where \( \mathcal{Y}_{PL}(E) \) is the is absolute magnitude of the photon flux detected outside the sample, \( \Delta \phi \) is the QFLS, \( E \) is the photon energy, \( k \) is the Boltzmann constant and \( T \) is the sample temperature. These values of calculated QFLS are tabulated in supplementary Table 1 and Table 2. It is to be noted that if \( \mathcal{Y}_{PL}(E) \) is not calibrated absolute QFLS may not be accurate. In this context we will focus only on the relative changes rather than absolute value of QFLS. To cross examine our result for reliability we have plotted \(-\ln(\mathcal{Y}_{PL}(E)/10^{23}E^2)\) versus \( \hbar \omega/kT \) and found that the slope is closed to unity (see Supplementary Fig. S10). It is interesting to see that the value of the QFLS at a least-bright point is 72 meV lower than the value of QFLS at the brightest point; this indicates the dark areas have higher trap-limited non-radiative recombination. This could be because of...
efficient hole extraction from smooth film and resulting in strong PL quenching and weaker hole extraction from micro-islands and giving rise to a weaker PL quenching which can be one of the reasons for heterogeneous PL emission across the film. Since, the distance between brightest and least bright points are within the charge carrier diffusion lengths in perovskites, we can say that the difference in PL intensity levels is most likely trap limited rather than diffusion limited which is consistent with the results published by DeQuilettes et al.\textsuperscript{22} Then we calculated the ratio of the integrated PL intensity from micro-island site (1) and non-island site (4) and found that the PL ratio is consistent with the widefield PL imaging and steady-state PL measurement, thus hyperspectral PL measurement also strengthen our speculation of improved light out-coupling because of MIs.

**SNOM imaging**

In our study of perovskite film, the grain size was close to the diffraction limit and it creates difficulty for widefield or hyperspectral PL imaging to probe the sub-grain heterogeneity. To probe the diffraction-limited region we performed SNOM having resolution less than 100 nm (pixel size 50 nm), Fig. 7 shows a PL intensity map taken by SNOM. Surprisingly we found that although the expected resolution of SNOM was lower than the grain size, we did not observe a PL contrast at the length scales of grain size due to larger diffusion length in perovskites. As suggested by DeQuilettes, et al. we can expect lower PL intensity at the grain boundaries.\textsuperscript{22} In another study by Yang, et al. they have shown that in CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} perovskite films the grain boundaries do not lead to increased recombination,\textsuperscript{49} rather non-radiative recombination may occur at the grain interior. Although, Yang et al. reported that the grain boundaries in their study were generally dimmer but the lifetime at the grain boundaries was not too worse as compared to the grain interior. We associate the absence of contrast at the length scale of grain size to the fact that in near field excitation diffusion process may dominate over the trap limited recombination at the grain boundaries, thus, our results are consistent with the findings of Yang, et al. Fig. 7c shows the PL spectra of four different tagged regions in Fig. 7a. The PL peak position is same for all the spectrum while the low energy tail states from low PL regions is slightly broader compared to the high PL regions, which is an indication of higher trap density. It indicates that the smooth funnelling of charge carriers from low defect locations to high defect locations quenches the PL intensity. Therefore, the dark regions (region iv) are quite large compared to the grain size in perovskite thin films.

**Photo-induced PL enhancement**

We have also observed overall PL enhancement (Fig. 8 and Supplementary Fig. S11) when samples are studied under a fluorescence microscope in ambient conditions. This is an important aspect as far as device efficiency or stability is concerned. This could be due to photocuring of perovskite nanocrystals in presence of oxygen as explained by Scheblykin group.\textsuperscript{56} Photo-induced PL enhancement is also attributed to the ion-migration by many researchers.\textsuperscript{57,58} For both the controlled and anti-solvent treated film, a PL enhancement is observed. The enhancement of PL intensity can be attributed to two simultaneously occurring processes. First it is due to a decrease in the concentration of defect sites (normally deep trap states) by photochemical reactions with oxygen and second process could be reduction in halide interstitial species and halide vacancy species because of the ion migration.\textsuperscript{57,58} Under light irradiation, Pb\textsuperscript{2+} oxidizes to PbO in Pb-clusters reducing their quenching activity. Alternatively, reactive oxygen species could passivate halide vacancies.\textsuperscript{59} We find that the PL enhancement is crystal geometry specific. PL enhancement in controlled films is faster in edges compared to the centre part of the micro-cube, that is because of the high surface to volume ratio near edges provides larger cross-section for oxygen diffusion from the environment to react and alter the photo physical properties of the material. Interestingly MIs show an overall decrease in PL intensity despite their higher surface area. This could be because of high carrier density leading to photo-induced degradation of the nanocrystals.\textsuperscript{56} However, PL enhancement is observed in smooth background film. This could be explained as the competition between photo-induced trap reduction and photo-induced trap generation. This type of
coexistence of light induced PL quenching and PL enhancement is very recently observed and explained by Haoran et al. They demonstrated that higher irradiation densities (higher $V_{oc}$) start to increase the photo induced trap generation rates and may dominate the photo induced trap reduction. QFLS is the measure of internal voltage which is responsible for ion migration. In our case we have observed higher QFLS at micro-island site and relatively low QFLS in smooth background film. Observation of photo-activation in background film is due to annihilation of Frankel defects, whereas as higher QFLS in micro-islands may create additional halide vacancies and result a photo darkening effect due to increase in defect densities with time. From Fig. 8 we can see that rate of photo-brightening (trap annihilation) is faster ($t_{bkg}^{\text{island}} = 39$ sec) compared to rate of photo-darkening ($t_{island}^{\text{island}} = 109$), that is why we observe a overall photo enhancement in our samples. The presence of both photoactivation and photodegradation in same film again indicates the presence of SK growth where both the stressed (non-island site) and relaxed regions (micro islands) are present. Photoactivation in non-island sites is possible because of the regions formed by FM growth mode creating more Frankel defects (interstitials species and vacancy species), while in the micro-islands formed by VW growth mode the stress is released and therefore these micro-islands are both stress and defect free.

**Electrical Characterization**

We have fabricated perovskite light emitting diodes (PeLEDs) in both p-i-n as well as n-i-p device structure. It has been observed that the overall device performance is significantly improved for the textured film as the active layer. The electroluminescence spectra (EL) show at least 7-fold increase in intensity for the textured film compare to smooth film (see Supplementary Fig. S13). However overall quantum efficiency was low due unoptimized device structure and also underestimated external quantum efficiency (EQE) measurement due to linear photodetector used to measure output photon flux. Further improvement in the device structure as well as interface engineering is thus needed to achieve high performance PeLEDs.

**Conclusions**

In summary, we have designed a textured morphology of perovskite film by optimizing the delay time for anti-solvent treatment. Stranski-Krastanov growth kinetics at low temperature can be realized in solution process perovskite film deposition. Our results identify that the presence of micro-island on smooth perovskite films can improve the PL emission by at least seven-fold. We studied the perovskite samples starting from long range to sub-grain resolution, using a widefield microscope, hyperspectral PL imaging, and SNOM technique. Widefield PL indicates that the heterogeneity in PL emission is mainly due to charge carrier confinement as well as trap limited recombination since the diffusion in widefield measurement is not limiting factor for PL intensity. By hyperspectral imaging, we have shown that the intensity variation in the PL spectrum for different regions of interest is due to the presence of multiple emitters, and the distribution of defect density. Estimated QFLS at the brighter point was found to be 72 meV higher compared to QFLS at low-intensity
regions. This indicates that the micro-islands do have high quantum yield, at the same time they help to improve the out-coupling efficiency by providing concave-convex geometry. Finally, with the help of SNOM, we have shown that the intensity variation in the background film is not diffusion limited, rather a trap-limited process. The strategy to minimize the bulk non-radiative sites can be the next step to achieve more homogeneous and high PL emission. We have also observed the photoinduced PL enhancement in perovskite micro-cubes as well as in smooth films, we believe this effect is a result of photo-induced curing of defect states due to reaction with oxygen related species and ion migration under light irradiation. However micro-islands show overall decrease in PL intensity which could be because of higher QFLS and generation of additional halide vacancies due to photo-induced ion-migration at micro-island sites. Overall device performance is also improved when the textured morphology is used as active layer.

Methods

Materials: All the chemicals were used as received, including Methylamine Solution (40%, Central Drug House Pvt. Ltd.), HBr (48%, Sigma-Aldrich), Ethanol (Analytical CS Reagent), Propan-2-ol (99.999% AR/ACS, SDFCl), N, N-Dimethylformamide (DMF, anhydrous 99.8%, Sigma-Aldrich), Dimethyl sulphoxide (DMSO) dried, SRL Chemicals), Chlorobenzene (extra pure AR, SRL chemicals), Benzylamine (99% Sigma Aldrich), Poly(3,4-ethylene dioxythiophene)-poly(styrene sulfonate) (PEDOT:PS). Conductive grade, Sigma-Aldrich), Lead bromide (99.9 Sigma Aldrich). MABr was synthesized by reacting 27.8 ml of aqueous HBr (48%, Sigma-Aldrich) with 44 ml of aqueous HBr (48%, Sigma-Aldrich) at 0 °C with continuous stirring in a conical flask for 4 hr. The solvent was removed and the precipitate was recovered by using rotary evaporation at 60 °C. The precipitate was then washed with diethyl ether to obtain a white MABr powder. Finally, the white powder was collected by filtration and dried at 60 °C in a vacuum oven for at least 24 h before use.

Device Fabrication: ITOs were cleaned following the standard procedure which is cleaning of ITO substrate by soap solution followed by sonication in distilled water, acetone, and IPA respectively each for ten minutes. After that, these substrates were exposed to UV-Ozone cleaning for 10 minutes. PEDOT: PSS (1.3 wt% dispersion in H2O) was further diluted in IPA as 1:1 and spin-coated on cleaned substrates at 5000 rpm for 60 seconds followed by annealing at 120 °C. For perovskite film coating, a controlled humidity chamber was used fixing the humidity at 25%, spin coating was done at room temperature (25 °C). Perovskite films were spin-coated on PEDOT: PSS coated ITO substrates. For perovskite coating we have followed an anti-solvent treatment method for controlling the crystallization of perovskite, therefore we have used chlorobenzene as an anti-solvent. Benzylamine was used as an additive to the anti-solvent by 0.5 wt%, 0.6M solution of CH3NH3Br and PbBr2 in a DMF/DMSO(7:3) co-solvent was used to deposit these films. For controlled films we deposited perovskite precursor solution by spin coating at 3000 RPM for 80 seconds, 5 seconds of acceleration time was given to achieve the maximum speed. For the antisolvent treated textured film, 120 µl of the anti-solvent solution was dropped at the 40th second of spinning whereas the plane film morphology can be achieved by dripping the anti-solvent at the 20th second of spinning. The experiment was performed multiple times to see the consistency in the result. Finally, these films were transferred to the hot plate maintained at 100 °C for annealing for 15 minutes. All the optical and structural characterizations are performed on these perovskite films directly coated on PEDOT: PSS. For device fabrication we spin coated 20 mg/ml, 2,2,2-(1,3,5-benzinetrityl)-tris-(1-phenyl-1-H-benzimidazole) (TPBI) solution in chlorobenzene. After spin coating TPBI, we transferred these devices to the thermal evaporator for electrode deposition, which is directly connected to nitrogen filled glovebox, finally 80 nm silver electrodes were deposited at 2x10^-6 torr at a deposition rate 1 Å/sec.

Characterizations

FESEM: The morphology and EDX of the perovskite samples were characterized by FE-SEM QUANTA 200 FEG Field Emission Scanning Electron Microscope.

AFM: INTEGRA, NT-MDT-INTEGRA instrument was used for AFM image acquisition. Large are scan (25 25 m2) is used to capture more number of micro-islands for calculation.

OPTICAL MICROSCOPE: Evos Fl inverted microscope with a 40X objective and GFP light cube was used for capturing optical images in optical and fluorescence mode.

HYPER SPECTRAL MICROSCOPY: Hyperspectral images were taken using a Photon Etc. IMA-VIS system. Both the samples were measured with the 100X Nikon air objective and a 405 nm continuous wave laser. The spectral measurements are performed by scanning the angle of the grating relative to the emitted light from the sample to form images at each wavelength which are stacked to form a data cube. The spectral resolution is in principle guided by the bandwidth of the holographic grating in the setup and is ~0.2 nm, although we have taken step sizes of 2 nm in this case. For spectral measurements 0.3 and 4 seconds integration time per wavelength is taken for anti-solvent treated and controlled film respectively and the light intensity was kept constant for all measurements.

SNOM-PL MAP ACQUISITION: For PL image acquisition an area of 5x5 µm2 has been scanned for 100 points per line and a 100 line scan has been used to construct the PL map. An integration time of 0.10495 seconds has been used to collect the PL signal. For PL mode microscopy a continuous wave LASER of 355 nm was utilized for sample excitation, whereas DUO420-OE 20432 CCD maintained at -59 °C was used to collect the PL spectrum. The spectral resolution of this setup is 0.13 nm.

X-RAY DIFFRACTION: The XRD spectrum was recorded on Bruker D8-Advance with a 0.54 Å monochromatic radiation. The spectrum was recorded from 5° to 55° with a step size of 0.02°.
EQE: External quantum efficiency was measured using a calibrated planner silicon photodetector directly placed on top of the LED.

Conflicts of interest
There are no conflicts to declare.

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Abbreviations
PeLEDs, Perovskite Light Emitting Diodes; SNOM, Scanning Near Field Optical Microscope; MIs, Micro-islands; GSV, grey scale value; ROI, region of interest.

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