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Shining a light on the photoluminescence behaviour of methylammonium lead iodide perovskite: Investigating the competing photobrightening and photodarkening processes

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Shining a light on the photoluminescence behaviour of
methylammonium lead iodide perovskite: Investigating
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processes

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Abstract

Organic-inorganic perovskite materials, such as methylammonium lead iodide, are good candidates for the next generation of solar cells with an impressive certified 23.3% power conversion efficiency. However, their development is impeded by their poor stability to oxygen, moisture, light and combinations of these. The bulk photoluminescence of perovskite films is extremely sensitive to the environment (humidity, light intensity, temperature, atmosphere) and has been shown to undergo rapid photobrightening and photodarkening processes. Here, we study the changes in photoluminescence behaviour (intensity, wavelength and full-width-at-half-maximum) in both air and nitrogen and correlate this with changes in the crystal structure of the films under illumination with XRD. We show that photodarkening is caused by degradation of the perovskite and that both brightening and some degree of darkening are competitive processes occurring simultaneously. During photobrightening the fluorescence emission spectrum red-shifts which can be explained by the halide redistribution and

passivation of trap states in the perovskite. We conclude that care is required when measuring fluorescence of perovskite due to the important variations in intensity, emission wavelength and full-width-at-half-maximum.

Keywords: photobrightening, photodarkening, perovskite, $\text{CH}_3\text{NH}_3\text{PbI}_3$, fluorescence, degradation

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1. Introduction

Perovskite solar cells (PSCs) have attracted great interest due to the remarkable increase of their power conversion efficiency (PCE) in only a decade, now reaching 23.3%[1]. In particular, hybrid organic-inorganic perovskites are attractive for use in photovoltaic devices due to their high absorption coefficient[2], high electron-hole diffusion lengths[3] and tuneable band gap[4]. However, stability issues need to be addressed; studies have shown that light, oxygen, moisture and combinations of these can degrade perovskites [5,6]. The degradation of methylammonium lead tri-iodide (MAPI) perovskite, which is commonly used in high efficiency devices[7], involves a distinct colour change from the brown/black MAPI to the yellow lead iodide (PbI_2)[5,6].

The study of the photoluminescence of perovskites provides important information regarding the electronic properties. The maximum fluorescence emission intensity (I_{max}) is a good indicator of the efficiency of radiative recombination, the maximum emission wavelength (λ_{max}) indicates the band-gap and the full-width-at-half-maximum (FWHM) is linked to the concentration of shallow trap states. MAPI is thought to contain a number of iodide vacancies and iodide interstitial point defects[8]. Upon illumination, photogenerated electrons are trapped in the positively charged vacancy-induced trap states thus neutralising it[9]. The resulting electric field drives the iodide interstitials out of the illuminated area, filling other traps[9]. This halide redistribution increases the fluorescence emission of the perovskite (photobrightening, PB) and could potentially reduce the hysteresis in PSCs[9]. Additionally, molecular oxygen can react with the photogenerated electrons to form superoxide[6]. This reaction has been shown to be more favourable in iodide vacancies which leads to the passivation of the trap states by superoxide[10]. Moisture also plays an important role in the passivation of trap states as it creates an amorphous nanometre-thin layer of degradation products at the surface of the perovskite grains, which is well known to have a higher concentration of “reactive” defects than the bulk[11]. Consequently, MAPI has been shown to photobrighten more in air than in a nitrogen (N_2) atmosphere due to the presence of oxygen, moisture and light compared to light only. However, oxygen and moisture are also known to degrade perovskite leading to a decrease of the photoluminescence (photodarkening, PD).

Photobrightening and photodarkening seem intrinsically linked, however it is not yet clear if these processes happen simultaneously or sequentially. Here, we attempt to answer this question through the study of the fluorescence and the X-ray diffraction (XRD) pattern of MAPI thin-films with time under constant illumination.

2. Methodology

MAPI thin films were spin-coated and characterised using X-ray diffractometry, fluorescence and UV-Vis spectroscopy and fluorescence microscopy under illumination in both air and N₂ as detailed in the Supplementary Information (**Figure S1 & S2**).

3. Results

In air, photobrightening of the sample is observed during the first 4 h of illumination followed by a quick photodarkening for *ca.* 3 h (**Figure 1a**). After 7 h of illumination, the sample was yellow which is characteristic of a degraded perovskite thin-film with only PbI₂ remaining. It is thus logical to associate this photodarkening behaviour to the degradation of the perovskite. During the photobrightening stage, the increase of the fluorescence intensity occurs with a decrease of the FWHM indicating the passivation of trap states in the film resulting in an increase of radiative recombination (**Figure 1d**).

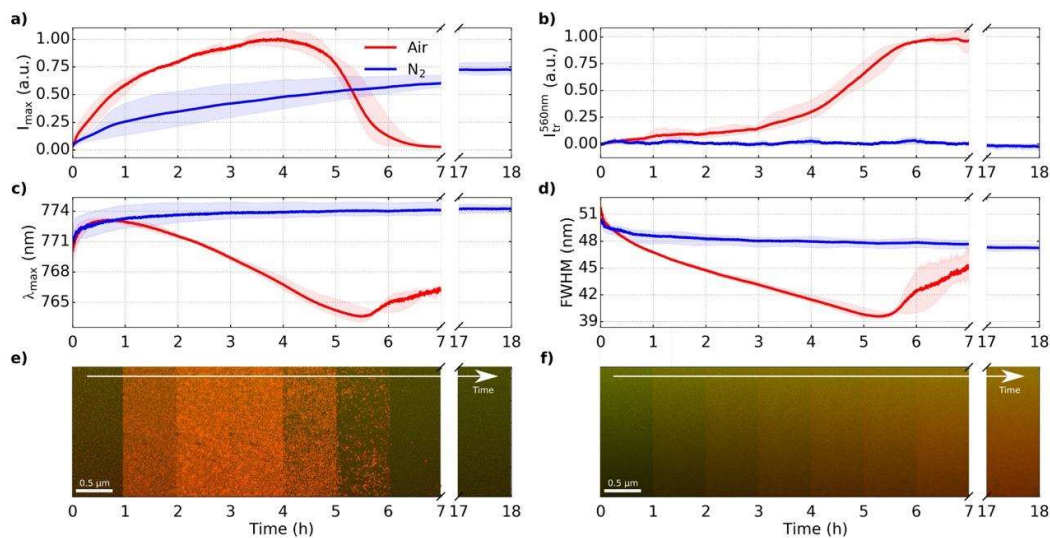


Figure 1: Fluorescence properties of MAPi thin-films under illumination in ambient conditions ($64 \pm 5\%$ relative humidity, $19 \pm 1^\circ\text{C}$) (red line) and N_2 atmosphere (blue line) (bold lines and coloured areas show the average of 3 samples and the standard deviation respectively) (See **Figure S3** for the fluorescence spectra). **a)** Maximum intensity (I_{max}), **c)** maximum emission wavelength (λ_{max}) and **d)** full-width-at-half-maximum (FWHM) of the fluorescence emission spectra **b)** transmitted intensity at 560 nm (I_{tr}) and fluorescence images of one sample in **e)** air and **f)** N_2 .

Towards the end of the photodarkening stage the FWHM begins to increase which we believe is due to an increased number of point defects associated with the advanced degradation of the film. The emission spectrum red-shifts quickly at the start and then blue-shifts after 1 h indicating a possible change in the perovskite band-gap (**Figure 1c**). A slight increase of the transmitted light (I_{tr}) is observed during the photobrightening phase, but it is only after the fluorescence reaches its maximum value that the transmitted intensity largely increases until it stabilizes after 6 h consistently with the degradation of the perovskite into PbI_2 (**Figure 1b**).

Photobrightening of the sample in N_2 is significantly slower and reaches a lower I_{max} than in air which is due to the absence of oxygen and moisture that can passivate trap states [10,11] (**Figure 1a**) confirmed by a smaller decrease of the FWHM (**Figure 1d**). The sample does not photodarken during the experiment and the absence of a visible colour and transmittance change suggest no degradation occurs. We conclude

that photodarkening observed in air is caused by the degradation of the perovskite. In N_2 , there is a similar red-shift to that observed in air over the first hour, no blue-shift is noted, hinting that the latter is linked to degradation of the perovskite while the red-shift is associated with the photobrightening (**Figure 1c**). Light slowly photobrightens the sample through trap state passivation and iodide migration consistent with previous observations[9]. Oxygen and moisture further participate to photobrightening through trap state passivation[11], however they also degrade the perovskite. It is therefore important to understand the order of these processes and indicate when photodarkening/degradation begins to occur.

The XRD pattern, absorption and the fluorescence spectra of a MAPI thin film under illumination were measured periodically (**Figure 2**). The amount of MAPI and PbI_2 was measured from the ratio of the [001] PbI_2 peak and [110] MAPI peak (**Figure 2a**).

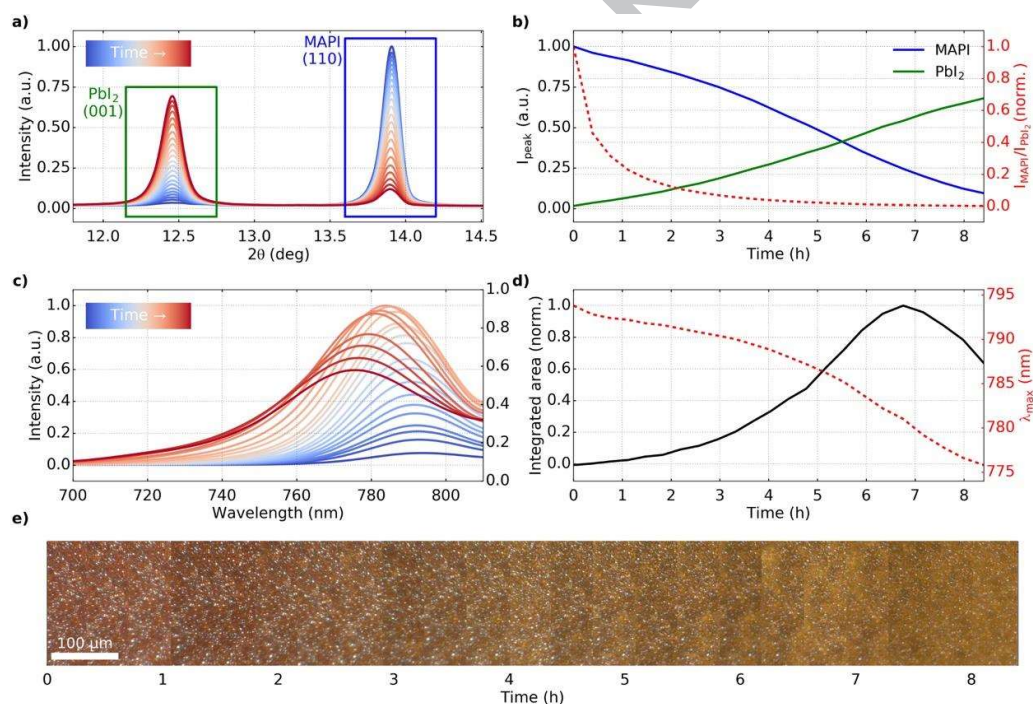


Figure 2: a) XRD pattern and **b)** MAPI and PbI_2 peak intensities and ratio, **c)** fluorescence spectra, **d)** integrated fluorescence area and λ_{max} of MAPI and **e)** optical microscopy images of the sample under illumination in air.

Under illumination, the MAPI peak intensity decreases while the PbI_2 peak increases (**Figure 2b**), consistent with the disappearance of the MAPI absorption front at 780 nm (**Figure S4**). Initially, there is

no colour change of the sample (**Figure 2e**). Despite the conversion of MAPI to PbI_2 we observe photobrightening, it is thus clear that degradation and photobrightening are competitive processes occurring simultaneously during illumination (**Figure 2d**). Without the degradation of the perovskite, we believe that the degree of photobrightening observed would be greater. In this experimental setup, no red-shift is observed due to the time between the first and second measurements.

4. Conclusion

Our results have shown that degradation (and thus photodarkening) can occur at the same time as photobrightening prior to an obvious colour change of the film. This suggests that degradation may occur earlier than previously thought as it is 'masked' by the photobrightening. Photobrightening is likely caused by the passivation of trap states (either by light and iodide migration or by oxygen and moisture) which leads to a reduction of the FWHM and a red-shift of the emission. Photodarkening is caused by the degradation of the perovskite possibly by oxygen and moisture and leads to a blue-shift of the emission and an increase of the transmittance.

Our results highlight that care should be taken when studying the photoluminescence of perovskites. There are a number of competing processes occurring at the same time which can be seen by the variation of the fluorescence maximum intensity, FWHM and maximum wavelength over time. This can lead to large variability in results which in turn impacts the understanding of these materials. Monitoring the photoluminescence over time should thus be favoured over single measures. Measurements in inert atmosphere may also be preferred as they inhibit the degradation of the perovskite, hence removing some of the competing processes.

Acknowledgments

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The authors declare no conflict of interest

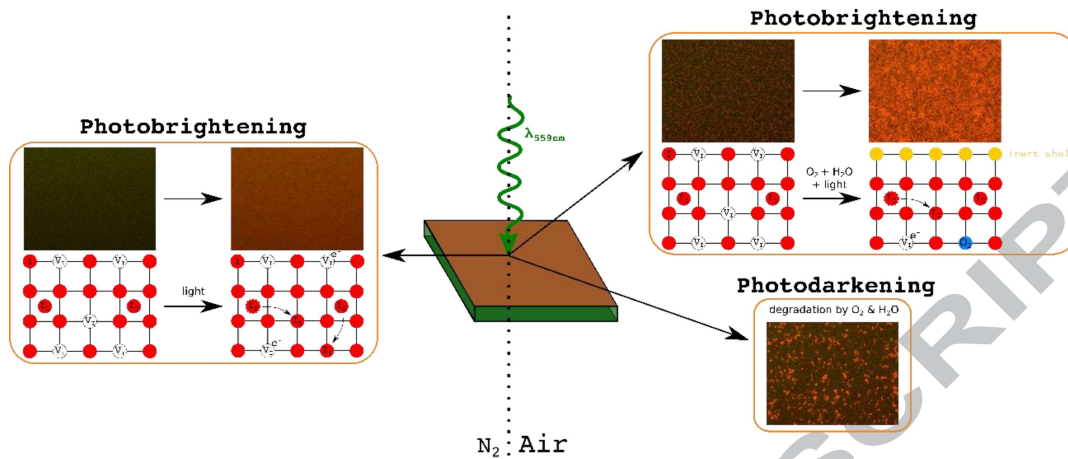
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Highlights

Study of the fluorescence properties of MAPI perovskite in air and nitrogen
Changes in fluorescence are correlated with morphology changes through XRD
Evidence that degradation occurs at the same time as photobrightening
Highlights the complex nature of fluorescence behaviour of perovskite thin-films



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