Photoluminescence Enhancement in Formamidinium Lead Iodide Thin Films
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Published in:
Advanced Functional Materials

DOI:
10.1002/adfm.201600715

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2016

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):
https://doi.org/10.1002/adfm.201600715

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Formamidinium lead iodide (FAPbI₃) has a broader absorption spectrum and better thermal stability than the most famous methylammonium lead iodide, thus exhibiting great potential for photovoltaic applications. In this report, the light-induced photoluminescence (PL) evolution in FAPbI₃ thin films is investigated. The PL intensity evolution is found to be strongly dependent on the atmosphere surrounding the samples. When the film is exposed to air, its photoluminescence intensity is enhanced more than 140 times after continuous ultraviolet laser illumination for 2 h, and the average lifetime is prolonged from 17 to 389 ns. The enhanced photoluminescence implies that the trap density is significantly reduced. The comparative study of the photoluminescence properties in air, nitrogen, and oxygen/helium environment suggests that moisture is important for the PL enhancement. This is explained in terms of moisture-assisted light-healing effect in FAPbI₃ thin films. With this study, a new method is demonstrated to increase and control the quality of hybrid perovskite thin films.

1. Introduction

Organic–inorganic halide perovskites have attracted great attention as a new class of light harvesting materials for developing low-cost and highly efficient solar cells.[1–3] In contrast to current commercial silicon solar cells, perovskite photovoltaics displaying high power conversion efficiency (>20%)[4–7] can be manufactured using low-temperature processing techniques. Despite the enormous advancements in device efficiency, stability and reproducibility of the device performances remain as a challenge.[8,9] Solution-processed perovskite solar cells are highly sensitive to processing conditions such as material composition, additives, concentration, temperature, and annealing environment.[10–16] A small variation of these conditions can lead to significant variations in power conversion efficiency even when following identical procedures. Moreover, often in the current–voltage characteristics of perovskite solar cells, an anomalous hysteresis is present.[17–19] This affects the stability of the power output under working conditions and leads to considerable error in evaluating real efficiencies. This hysteresis has been speculated to originate from trapping/detrapping of charge carriers within or near the surface, ferroelectric properties of hybrid perovskite ion migration.[18,20,21]

The photophysics of perovskite thin films and their device performance have been shown to change upon illumination in a number of recent publications.[22–27] It was discovered that a new, red-shifted peak appears in the photoluminescence spectra of mixed-halide hybrid perovskites under 1-sun illumination.[23] The carrier diffusion length in MAPbBr₃(Cl)-based solar cells was demonstrated to increase about 3.5 times upon laser illumination.[28] The open-circuit voltage and fill factor of solar cells were reported by Hu et al. to continuously increase with illumination while the short-circuit current experiences a fast increase and then a decrease upon further light exposure.[29] These illumination-induced variations of the device performance suggest that important light-induced processes are occurring in the active material. It is therefore important to study these phenomena to improve the performance and stability of hybrid perovskite photovoltaic devices.

Formamidinium lead iodide (FAPbI₃) is a relatively, newly developed perovskite material that can potentially provide better performance than methylammonium lead iodide (MAPbI₃) because of its narrower bandgap, which allow absorption of photons over a broader range.[6,7,29–32] Moreover, FAPbI₃ exhibits negligible hysteresis during current-voltage measurements.[31,34]

In this work, the room temperature photophysical properties of FAPbI₃ thin films under different environments are investigated. We observed light-induced enhancement in the photoluminescence intensity when samples are exposed to air while under continuous ultraviolet light illumination. The role of nitrogen and oxygen on the photophysical properties of the film is further investigated. We demonstrated that moisture plays a fundamental role in the light-healing effect in FAPbI₃ thin films.

2. Results and Discussion

FAPbI₃ perovskite thin films were deposited on FTO-coated glass substrates by spin-coating from equimolar mixtures of
FAI and HPbI$_3$ precursors in N,N-dimethyl formamide.\textsuperscript{[12]}

The thin films are fabricated in a nitrogen-filled glove box. The detailed device fabrication procedure is described in the Experimental Section. The phase purity of the thin films is confirmed by the X-ray diffraction pattern. The room temperature photoluminescence spectrum is centered at 820 nm.

To investigate light-induced effects on the photophysical properties of FAPbI$_3$ thin films, the second harmonic (≈400 nm wavelength) of a mode-locked Ti:Sapphire laser (Mira 900, Coherent) was used as illumination source. The laser pulses were operated at 76 MHz, and were focused with a 150 mm focal length lens into around 100 µm in diameter. The illumination power density was about 6 µJ cm$^{-2}$. The evolution of the PL spectra was monitored by a spectrometer equipped with a Si CCD camera. For the PL measurement, the same laser is used as excitation source. Figure 1a displays the 3D representation of the photoluminescence spectra as a function of the illumination time in ambient condition (humidity of 60%). Upon illumination, there is a first ($t < 18$ min) increase of the PL intensity with a subsequent decrease ($18 < t < 25$ min), followed by a new constant increase ($25 < t < 120$ min) of intensity. The time-dependent photoluminescence spectra illustrated in 2D pseudocolor plot (Figure 1b) shows that the emission peak wavelength does not shift with time. Figure 1c shows the PL spectra collected at different times, demonstrating that no change in the spectral shape takes place, showing that the emission peak wavelength does not shift with time. Figure 1d shows the PL intensity evolution becomes evident when it is plotted as a function of illumination time and the PL intensity normalized with respect to initial intensity as depicted in Figure 1d. The $I_t/I_0$ increases till a maximum of 130 followed by a slight intensity drop, which subsequently stabilizes for about 30 min before gradually increasing to more than 140.

The strong increase of the PL intensity in the illuminated area suggests a light-induced passivation effect of trap-states, which mediates nonradiative recombination. Time-resolved PL (TRPL) measurements performed on the pristine samples and the one illuminated under ambient condition are shown in Figure 2. While the pristine sample displays a PL lifetime of approximately 17 ns, the average lifetime for the laser-illuminated area is about 389 ns, with a fast component fitted with $t_1 = 57$ ns and a slow component with $t_2 = 667$ ns. The steady state and time resolved PL measurements both indicate that the nonradiative recombination channels are greatly inhibited and the number of defects is significantly reduced upon laser illumination under ambient conditions.

At this point the question arises: why is the photoluminescence greatly enhanced? Is it because of spontaneous defect...
annihilation as was recently demonstrated in CH$_3$NH$_3$PbI$_3$,
[35] or is due to the same mechanism that induces light soaking
effects in solar cells?[20] Here, it is important to note that in
the unilluminated parts of the film there is no giant PL inten-
sity enhancement observed, suggesting that the reported
spontaneous defect annihilation cannot explain the observed
phenomena. On the other hand, the reported PL intensity
enhancement due to light soaking in perovskite solar cells
is only 2–3 times, which is much lower than the 140 times
reported here.[20]

In order to gain further insight into the underlying mecha-
nism, we encapsulated the films in a N$_2$-fi lled glove box with
an epoxy adhesive and a 0.5 mm coverslip to investigate the
photophysical properties of the air-isolated samples. Figure 3a
shows the PL spectrum of the encapsulated film at selected
times under the excitation of constant laser power of 6 µJ cm
$^{-2}$, while Figure 3b illustrates the evolution of the PL intensity with
time. The comparison of these measurements with the one of
the unencapsulated films points to several important differ-
ences. First, there is no spike or drop in the PL evolution in the
encapsulated film. The PL intensity constantly increases with
time. Second, the PL intensity variation in the encapsulated
film is much smaller, with an increase of less than two times
after 2 h of illumination. These marked differences between
air-exposed and isolated films suggest that the presence of a
variety of gases and molecules in the atmosphere may account
for the observed enhancement of the PL under ambient con-
ditions. In particular, the combined effect of the atmosphere
components and the illumination appear to be responsible for
the PL enhancement.

To distinguish the role of different gases on this light-induced
PL enhancement phenomenon, the experiments were repeated
keeping the unencapsulated fresh samples in a chamber fi lled
with dry nitrogen and in a mixture of oxygen and helium (1:4).
Figure 4a,b shows the evolution of the photoluminescence intensity
as a function of the illumination time under the same laser
power illumination in nitrogen and oxygen/helium environ-
ment, respectively. The PL intensity in both cases fi rst increases
2–3 times to reach a maximum and then drops under prolonged

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Figure 2. Time resolved photoluminescence measurement for FAPbI$_3$
thin fi lm at exposure $t = 0$ and after 120 m illumination in ambient
condition.

Figure 3. a) Photoluminescence spectra of encapsulated FAPbI$_3$ thin fi lm
at selected time under continuous laser illumination; the laser wavelength
was 400 nm and the power density was 6 µJ cm$^{-2}$. b) Evolution of the
photoluminescence intensity under constant laser excitation. The emis-
sion intensity increases of less than two times during 2 h laser exposure.

Figure 4. Evolution of the photoluminescence intensity as function
of illumination time under a) nitrogen and b) oxygen/helium (1:4)
environment. The laser wavelength was 400 nm and the power density
was 6 µJ cm$^{-2}$. 

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illumination. In the case of the sample kept in an oxygen/helium mixture, the intensity increases to its maximum within approximately 23 min; while in dry nitrogen, it takes around 40 min.

Photoactivation and deactivation of the PL emission in perovskite films have been recently reported in a number of publications.\(^{[22,36]}\) It has been suggested by Míguez and co-workers that luminescent properties of MAPbI\(_3\) are determined by the interplay between photoinduced activation and darkening processes.\(^{[36]}\) The authors related the photoactivation to the filling of sub-gap trap states, while the strong photodarkening is mainly due to the presence of moisture in the atmosphere. In FAPbI\(_3\), the photodarkening process is much weaker than that of MAPbI\(_3\). The PL intensity is significantly increased under ambient conditions (140 times) compared to when measured in oxygen and nitrogen (2–3 times). This suggests that moisture aids in the defect passivation in FAPbI\(_3\) during the illumination process. Moreover, we find that the PL intensity does not decrease after the sample have been kept in dark and in vacuum for 3 h (see Figure S1, Supporting Information), which is substantially different from light soaking effect reported in MAPbI\(_3\) solar cells. The PL enhancement here is an irreversible process.

It has been reported by several groups that prolonged exposure to moist air degrades methylammonium lead iodide perovskite films due to disruption of their crystalline structure in the presence of excess water.\(^{[29,37–40]}\) Nevertheless, some reports demonstrated that moisture is beneficial to the crystallization process and therefore increases the device performance.\(^{[12,41,42]}\) In other reports, by annealing the film in air, an improved crystallinity and large-grain domains are formed as compared to the same process in a nitrogen environment, and also, that efficient solar cells can be fabricated in ambient conditions.\(^{[12,43]}\) We therefore investigated the evolution of the photoluminescence intensity of the film in air under different excitation powers (see Figure S2, Supporting Information). In contrast to what occurs in nitrogen and oxygen environment at the excitation density of 6 \(\mu J\) cm\(^{-2}\) (only a factor of 3 enhancement), an enhancement ratio higher than 30 times was observed even at excitation power density as low as 32 nJ cm\(^{-2}\). We posit that the moisture plays an important positive role in our case, which triggers the possibility for light-induced defect passivation with a consequent healing of the trap states. The PL enhancement is determined by the interplay between the moisture-assisted light-healing effect and degradation effect, and strongly dependent on laser power. When the film is exposed to moisture in the dark or at very low illumination powers (below 32 nJ cm\(^{-2}\)), a new emission at around 760 nm (possibly from PbI\(_2\)) is observed after 2 h of exposure, suggesting the degradation of the material. This new emission is absent when the excitation power is higher than 32 nJ cm\(^{-2}\) (see Figure S3, Supporting Information).

The next question is whether the perovskite film is homogeneously healed by the laser. To clarify this point, we performed confocal laser scanning microscopy (CLSM). For these measurements, an Ar\(^+\) laser (488 nm) was used as excitation source for the illumination and to investigate the light-induced photoluminescence imaging evolution. Figure 5 shows the confocal fluorescence microscopy images of FAPbI\(_3\) thin film under the Ar\(^+\) laser illumination at different times. The illuminated area was raster scanned at a rate of 5 \(\mu s\) per pixel. In comparison to the initial image (shown in Figure 5a), the brightness after 1 h illumination (Figure 5b) is significantly increased, suggesting that the defects in the film are passivated (see Figure 1 and discussion therein). Besides the change in PL brightness, we can find a substantial inhomogeneity of the brightness of different domains. After extended illumination, some bright parts of Figure 5b image became dark, as shown in Figure 5c,d. We attribute this to the partial degradation of FAPbI\(_3\) due to an excess of water, and it is dependent on the laser wavelength and power density deposited per unit surface. As mentioned earlier, when considering the impact of moisture on perovskite film, it is important to distinguish its role on formation and on degradation. Exposure of the film to air without laser illumination results in color change in some regions of the film from black to yellow within 30 min. Thus, excess moisture plays a negative role in deforming the crystal structure. However, when the film is illuminated with a high-energy light, as in our case, a suitable amount of moisture is positive and helps promoting the laser-induced defect passivation. It can be argued that the
effect of light is to locally heat the film, inducing a local crystallization. However, we noticed that the healing effect is much weaker when the film is illuminated with 605 nm or with IR light (see Figure S4, Supporting Information) than with UV and blue laser under the same power conditions. Thus, the PL enhancement cannot be ascribed to the heat deposited by the laser, but most probably to the passivation of the defects by the high-energy light, as observed in inorganic semiconductor nanocrystals. The illumination by high-energy light causes surface transformations in FAPbI₃, leading to trap state passivation. The light-deposited heat, to some extent, can protect the FAPbI₃ from degradation; the UV light can further passivate the defects in the films. The film quality and physical properties are determined by the interplay between moisture degradation and moisture-assisted light healing, and thus are correlated with humidity level and light power.

To better understand the origin of these findings, the evolution of the film was monitored with X-ray diffraction (XRD) while being exposed to air. In order to illuminate the whole thin film, an UV-light lamp with power of 200 W is used to illuminate the film (5 mW cm⁻²). Figure 6a shows the schematic of the XRD experiment performed on the thin film under UV illumination in ambient conditions. In Figure 6b, XRD patterns of FAPbI₃ thin film under illumination of UV light in air at different times are presented. The as-prepared FAPbI₃ perovskite film exhibits high crystallinity with strong (110) preferred orientation (corresponding to the 13.9° peak). The patterns are maintained during the 2 h experimental process. When examined closely, the peak corresponding to the (001) plane of PbI₂ at 11.5° in the zoomed XRD pattern (Figure 6c) does not increase after the UV light exposure in air.

Similarly, we also investigated the thin films exposed to ambient condition in the absence of UV light illumination. A comparison between the fresh thin film and 1 h exposed sample is shown in Figure 6d. Strong evidence of degradation of FAPbI₃ was found after an hour of exposure to air. The FAPbI₃ (110) peak intensity decreased by 85%, while the peak from PbI₂ became dominant. The presence of PbI₂ can be recognized by reflections at ≈11.5° and 26.2°, showing the formation of PbI₂ crystallites in the film when exposed to ambient conditions. Thus, the UV-light exposure is crucial for suppressing the thin film degradation. This is a further confirmation that the illumination with UV light is important to improve the quality of the films.

Figure 6. a) Schematics of the XRD measurements performed on thin film under illumination of UV light in humid air. b) XRD patterns of FAPbI₃ thin film under illumination of UV light in humid air at different times. c) Enlarged XRD pattern showing that the diffraction peak for PbI₂ is suppressed. d) Comparison of the XRD pattern recorded in fresh thin film and in films exposed 1 h to ambient conditions (the film was not illuminated). After exposure to air strong diffraction from PbI₂ is recorded.
3. Conclusion

In summary, the light-induced photoluminescence enhancement in hybrid FAPbI$_3$ has been investigated. By exposing FAPbI$_3$ films to ambient conditions while being illuminated by UV laser, we observed that the photoluminescence intensity can be enhanced more than 140 times. In nitrogen and oxygen environment, the PL is only increased by a factor of 2–3 times, followed by degradation. The comparative study of the photoluminescence properties in different environment suggests that a suitable amount of moisture is necessary for defect passivation. Further evidences show that high-energy light (UV and blue light) is much efficient than low energy light (red and IR light) to heal the thin films. Thus, using an UV light with suitable power can passivate defects and suppress nonradiative recombination in FAPbI$_3$ thin films. This finding opens a new direction in the fabrication of defect-free hybrid perovskite films and improvement of solar cells.

4. Experimental Section

Materials: FAPbI$_3$ perovskite films were prepared from a mixture of formamidinium iodide (FAI) and HPbI$_3$. FAI and HPbI$_3$ were dissolved in anhydrous DMF at a molar ratio of 1:1. Perovskite thin film deposition was carried out in a glovebox under dry nitrogen atmosphere. The solution was spin-coated on a clean glass substrate at 3000 rpm for 60 s. The sample was immediately annealed at 100 °C for 10 min to evaporate residual solvent and further at 160 °C for 80 min to promote crystallization. Encapsulated films were sealed with a blank glass using epoxy adhesive (Epo-Tek OG 159-2).

Spectroscopic Measurement: Photoluminescence measurements were performed by exciting the samples with the second harmonic (about 400 nm) of a mode-locked Ti:Sapphire laser (Mira 900, Coherent). The laser power was adjusted using neutral density filters. (about 400 nm) of a mode-locked Ti:Sapphire laser (Mira 900, Coherent). The laser power was adjusted using neutral density filters. The spectrum was corrected for the spectral response of the set up. For the light-induced photoluminescence intensity evolution, five batches of samples (2-3 samples for each batch) have been tested. Identical photoluminescence enhancement is observed in all samples. Time-resolved traces were recorded with a Hamamatsu streak camera working in single sweep mode. The excitation source was the same mode-locked femtosecond laser with a repetition rate of 76 MHz; a pulse picker was inserted in the optical path to decrease the repetition rate of the laser pulses when needed. For the investigation of excitation wavelength effect, a supercontinuum laser (NKT Photonics) equipped with acusto-optical wavelength selection was used as excitation source. Confocal laser scanning microscopy measurements were performed with a Nikon (Tokyo, Japan) Eclipse Ti microscope in backscattering configuration. A Nikon 40x Plan Apo objective lens was used for all the images reported. The excitation source was an Ar+ laser (excitation wavelength at 488 nm). The photoluminescence images of the samples were recorded reconstructing the photoluminescence intensity point by point (1024 x 1024 pixels).

X-Ray Diffraction Measurements: XRD measurements on thin films were performed with a Rigaku ru-300 diffractometer using Cu K$_\alpha$ irradiation (λ = 1.5406 Å). During the XRD measurements, the samples were exposed to ambient conditions (25 °C, 60% RH). In order to investigate the effect of light exposure on the samples, an UV laser (IntelliRay-400) with average power of 200 W and wavelength centered at 415 nm was used to illuminate the whole film during the measurements. The excitation power at film surface is around 5 mW cm$^{-2}$. The XRD patterns were acquired by recording at a standard 2θ step size of 0.01° and a scan speed of 15° min$^{-1}$.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The Groningen team would like to acknowledge funding from European Research Council (ERC Starting Grant “Hy-SPOD” No. 306983) and the Foundation for Fundamental Research on Matter (FOM), which is part of the Netherlands Organization for Scientific Research (NWO), under the framework of the FOM Focus Group “Next Generation Organic Photovoltaics”. S. Adajokatse acknowledges financial support from NWO Graduate School funding. N. Zhao would like to acknowledge the Theme based Research Scheme grant (723-407/13-N) from the Research Grants Council of Hong Kong. The technical support of A. Kamp is highly appreciated. The authors would like to thank T. M. Palstra and Jacky Even for valuable discussions.

Received: February 8, 2016
Revised: March 9, 2016
Published online: April 18, 2016