Investigating the Effect of Pyridine Vapor Treatment on Perovskite Solar Cells

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Abstract

Perovskite photovoltaics have recently come to prominence as a viable alternative to crystalline silicon based solar cells. In an effort to create consistent and high-quality films, we studied the effect of various annealing conditions as well as the effect of pyridine vapor treatment on mixed halide methylammonium lead perovskite films. Of six conditions tested, we found that annealing at 100°C for 90 minutes followed by 120°C for 15 minutes resulted in the purest perovskite. Perovskite films made using that condition were treated with pyridine for various amounts of time, and the effects on perovskite microstructure were studied using x-ray diffraction, UV-Vis spectroscopy, and time-resolved photoluminescence lifetime analysis (TRPL). A previous study found that pyridine vapor caused perovskite films to have higher photoluminescence intensity and become more homogenous. In this study we found that the effects of pyridine are more complex: while films appeared to become more homogenous, a decrease in bulk photoluminescence lifetime was observed. In addition, the perovskite bandgap appeared to decrease with increased pyridine treatment time. Finally, X-ray diffraction showed that pyridine vapor treatment increased the perovskite (110) peak intensity but also often gave rise to new unidentified peaks, suggesting the formation of a foreign species. It was observed that the intensity of this unknown species had an inverse correlation with the increase in perovskite peak intensity, and also seemed to be correlated with the decrease in TRPL lifetime.

Introduction

Solar photovoltaics are an important form of clean energy, and cells made of crystalline silicon dominate the commercial PV market. However, the performance of crystalline silicon has remained relatively constant for decades; the possibility of creating cheaper and more efficient cells motivates scientists to continue searching for alternative materials. Perovskites are a class of materials whose crystal structure has the formula ABX_3, where X is a halogen or oxygen[1]. These substances have emerged as one of the newest and most promising solar cell materials: they have seen incredible efficiency gains in just a few years, jumping from 3.8% in 2009 to over 20% in 2014[2]. Of the many possible types of perovskite, organometallic halide perovskites are often studied in the context of photovoltaics. Specifically, perovskite materials with the formula $CH_3NH_3PbCl_xI_{3-x}$ were investigated in this study.

A further advantage is that perovskites can be manufactured using a fairly simple procedure. A solution is prepared, spin coated onto a substrate, and the films are annealed. It is known that the annealing conditions—that is, both temperature and amount of time—are extremely important[3], since annealing is responsible for the actual chemical reaction that forms perovskite:

$$CH_3NH_3I + PbCl_2 \rightarrow CH_3NH_3PbCl_xI_{3-x}$$

Methylammonium Iodide + Lead (II) Chloride → Perovskite
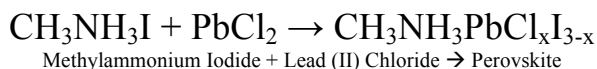
Despite a growing body of work on perovskite solar cells, the processes for making high-quality perovskite are neither fully understood nor consistently applied. The annealing conditions reported in existing literature vary widely. This could give rise to inconsistencies in the quality of perovskites being used to conduct research. Thus, it would be valuable to clarify which annealing conditions are most effective.

Researchers are also exploring how various post-production treatments could further enhance perovskite efficiency. A recent paper, published by Ginger *et al.* details the impact of pyridine vapor treatment on perovskite microstructure[4]. It has previously been noted that a high photoluminescence (PL) lifetime is associated with a more efficient film[5]. This paper reports that perovskite films are not homogenous—PL lifetimes and intensities vary between different grains of the same film. Exposure to pyridine vapor caused the film to become brighter (that is, exhibit greater PL) and more homogenous, indicating the potential to enhance the overall performance of the film. We sought to understand why pyridine has this effect and study how it interacts with the perovskite material on a structural level. We employed three different tests to study pyridine's effects. The first is time-resolved photoluminescence (TRPL) testing, which characterizes carrier lifetimes by measuring the decay in PL as a function of time[6], similar to the measurements presented by Ginger *et al.* The second test is UV-Vis spectroscopy, which measures how the material's absorbance varies with wavelength of light, and allows us to extract information like the bandgap of the material. The third type of test was wide-angle x-ray diffraction (XRD) in reflection geometry. XRD reveals the type and concentration of crystalline species present, which is useful in detecting structural changes.

Methods

Sample preparation
A solution was synthesized using a standard recipe of a 3:1 ratio of methylammonium iodide (MAI) and lead (II) chloride dissolved in N,N-dimethylformamide[7]. The resulting perovskite precursor solution was stirred for ~12 hours at room temperature. Glass substrates were prepared using standard microscope slides cut into $1cm^2$ pieces. Each was sonicated in successive solutions of soapy water, water, acetone, isopropanol, and deionized water for 5 minutes each. The cleaned substrates were blown dry and baked at over 100°C on a hot plate inside a nitrogen glove box. Perovskite precursor solution was deposited as a thin film onto substrates using a spin coater in the same glove box. Each substrate was transferred from the hot plate directly to the spin coater, 30 μL of solution were pipetted onto the substrate, and spin coating was carried out for 1 minute at 2000 rpm with a ramp-up acceleration of 12000rpm. The resulting films rested for 30 minutes in the nitrogen glove box, and then were annealed in a dry glove box. During initial runs, various annealing conditions were tested; for pyridine treatment, annealing conditions of 100°C for 90 minutes followed by 120°C for 15 minutes were used. Temperatures were measured with a small thermocouple placed next to the samples, which rested on top of a copper block on a hot plate. A batch of 8 samples was prepared for the pyridine study; two samples were treated with pyridine vapor for 5 minutes, two at 20 minutes, two at 60 minutes, and two were used for a separate in-situ study. Pyridine vapor treatment was conducted at room temperature by placing perovskite on a cap in a petri dish filled with ~1 ml pyridine diluted in chlorobenzene in a1:10 ratio and half-covering the setup.

X-ray Diffraction
Grazing incidence wide-angle x-ray scattering was performed at beamline 11-3 at the Stanford Synchrotron Radiation Lightsource (SSRL). The beam was calibrated using a LaB_6 standard. Data was collected for each sample using an incidence angle of 2.5° and an exposure time of 20 seconds, and re-measured at 3 seconds if the 2D image showed oversaturation. The resulting

diffraction data was normalized with respect to incoming flux and time, and processed using GSASII software.

<u>UV-Vis Spectroscopy</u>
Measurements were conducted at SSRL. The tool used did not have an integrating sphere, leading to systematic error in calculating absorbance. Two spots per sample were scanned between wavelengths of 300 and 1000 nanometers, and a background correction was applied based on the transmission data for plain glass. The data was further processed to approximate the contribution of scattering; the corrected absorption values were scaled by light energy and plotted against energy to obtain Tauc plots for each curve. A linear fit was obtained for the portion of the curve near the onset of absorption, which allowed for calculation of bandgap (relative values).

<u>Time Resolved Photoluminescence</u>
TRPL tests were conducted at Stanford University in the Brongersma lab. Measurements were obtained for three spots on each sample; each test was conducted for two minutes, with a pulse occurring every 400 nanoseconds. A single exponential curve was fit to the resulting data to obtain a value for the lifetime.

Results and Discussion

<u>Annealing Conditions</u>
X-ray diffraction data was obtained for six different annealing conditions (100°C for 1.5 hours, 100°C for 2 hours, 100°C for 2.5 hours, 100°C for 1.5 hours followed by 120°C for 5 minutes, 100°C for 1.5 hours followed by 120°C for 10 minutes, and 100°C for 1.5 hours followed by 120°C for 15 minutes), and the resulting 1D curves were superimposed on a reference curve of pure perovskite. It was found that 100°C for 1.5 hours followed by 120°C for 15 minutes produced peaks that most closely matched this reference, as shown in Figure 1. When conducting the pyridine study, we ensured that all samples were processed using this annealing condition.
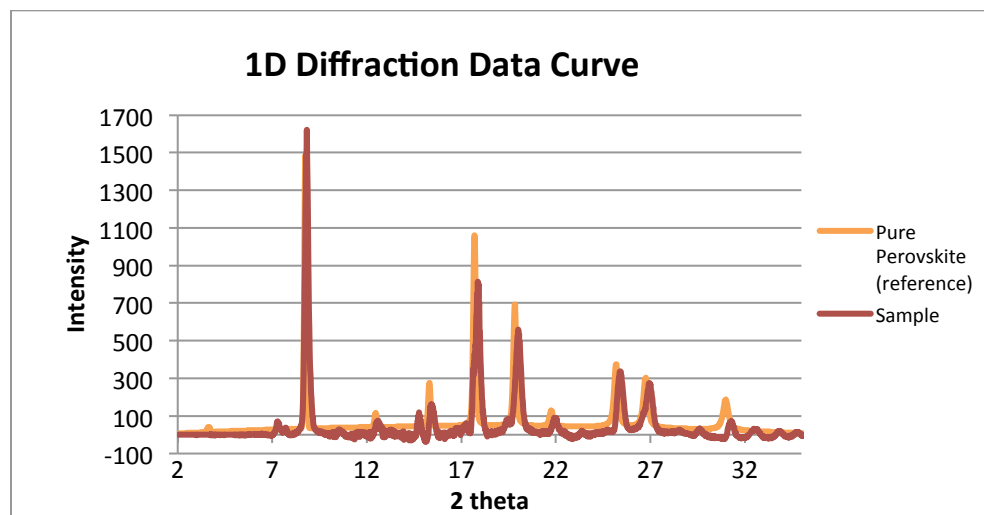

Figure 1: 1D diffraction curve from annealing conditions of 100°C for 1.5 hours followed by 120°C for 15 minutes, superimposed on pure perovskite reference curve.

<u>Pyridine Vapor Treatment</u>

Perovskite performance is highly dependent on a variety of factors, and the material is sensitive to both water and air. To control the experiment as much as possible, all samples used for pyridine treatment were synthesized at the same time using the same procedure. As shown in Figure 2b, all had good lifetimes, and all except sample 6S yielded a good diffraction pattern. Notably, though, the pre-treatment lifetimes still varied by several hundred nanoseconds.

In conducting the three separate tests, we noted several interesting trends among the data, some of which seemed to contradict each other. Figure 2a shows an example of the raw data obtained from the TRPL test; fitting a single exponential to this data gave us a single lifetime value. As shown in Figure 2b, the TRPL lifetimes of samples after pyridine treatment showed relatively little spread compared to the values before treatment; this would tend to suggest that pyridine has indeed made films more homogeneous. However, all TRPL values after pyridine treatment are lower than the TRPL values before treatment. This decrease in lifetime seems to contradict the claim that pyridine vapor enhances PL intensity and carrier lifetime. Examining the UV-Vis as well as the XRD data provide more information, and ultimately a possible explanation for this phenomenon.
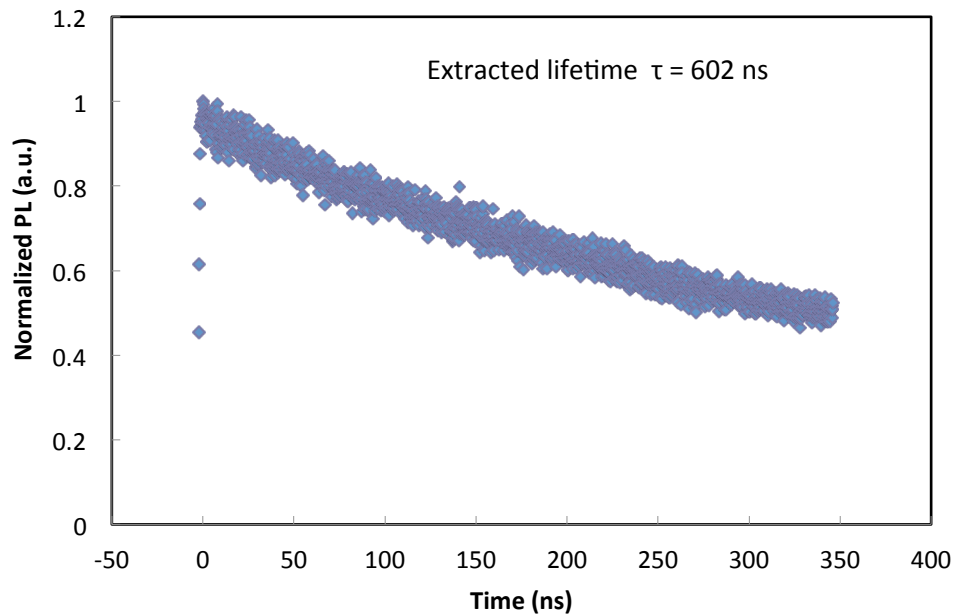

Figure 2a: TRPL data obtained for a sample before treatment.
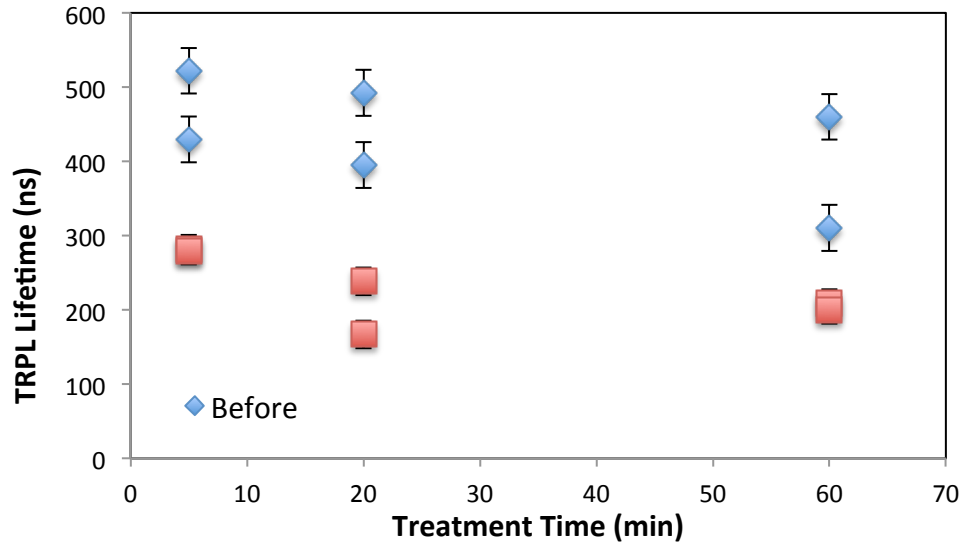
Figure 2b: TRPL lifetime values before pyridine treatment (blue) and after pyridine treatment (red), plotted against length of pyridine treatment time.

We can analyze the UV-Vis spectroscopy data by transforming them into Tauc plots for direct bandgap materials[8] (an example is shown in Figure 3a), from which we can extract a value for the bandgap of the film. Due to the limitations of the tool used, the effects of scattering were not adequately taken into account. Therefore, the extracted bandgap values can only be taken as relative, not absolute, numbers. Regardless, a trend is still clear: comparing the values of the bandgap before and after pyridine treatment reveals that increased pyridine treatment time seems to decrease bandgap slightly, as shown in Figure 3b. While there are many features that could contribute to a decreased bandgap, a likely explanation is an introduction of more trap states, which would also be associated with lower PL lifetime.
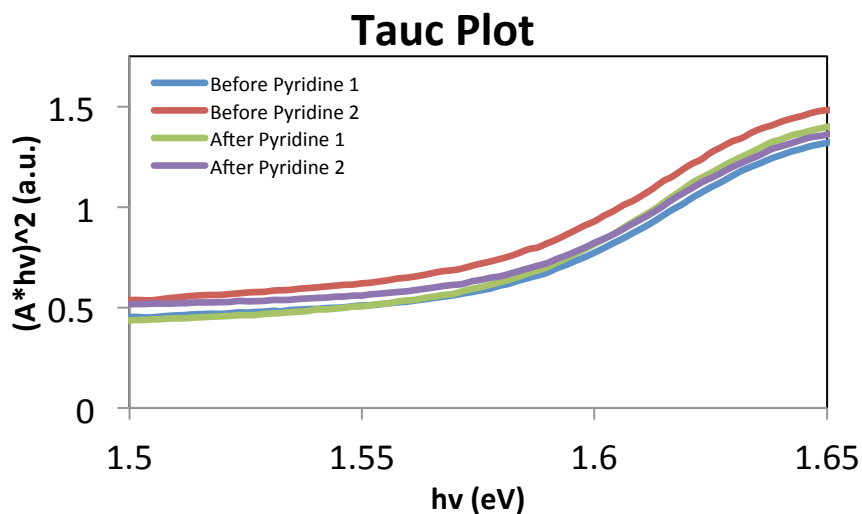

Figure 3a: Tauc plot with curves for the samples before treatment (red and blue) and after treatment (green and purple) superimposed.
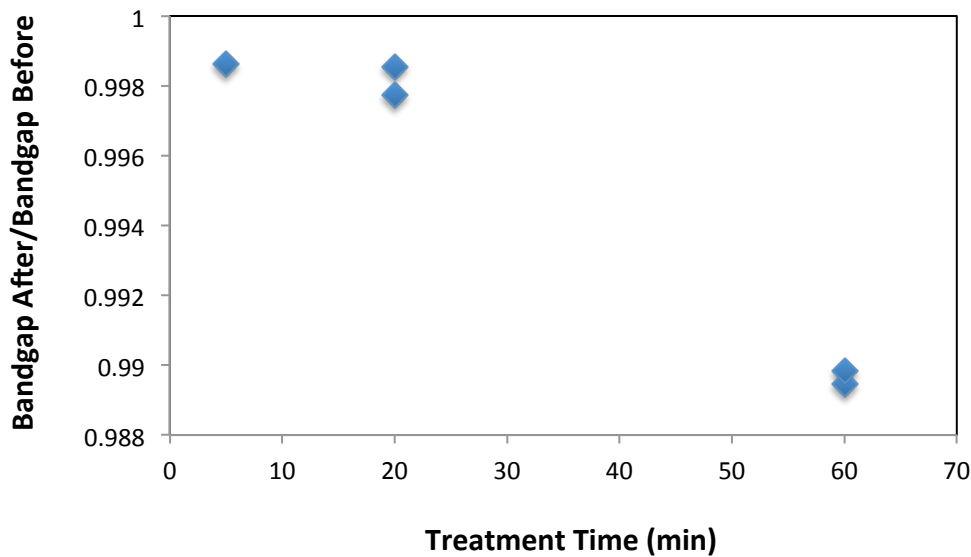
Figure 3b: Ratio of bandgap after pyridine treatment to bandgap before pyridine treatment, plotted against length of pyridine treatment time.

XRD analysis allows for examination of pyridine's effect on a structural level. As shown in Figure 4a, exposure to pyridine increased the (110) perovskite peak area for all samples, suggesting an increase in the degree of crystallinity of the film overall. At the same time, the 1D curves from pyridine treatment revealed an unexpected effect: some new peaks appeared that didn't correspond to perovskite or either of the reactants, as highlighted in Figure 4b. While we cannot be sure about the identity of this species, we suspect it may arise from pyridine interacting with either trace reactants or incorporating into the perovskite itself. The presence of this new species provides a possible explanation that ties together our other seemingly contradictory trends.
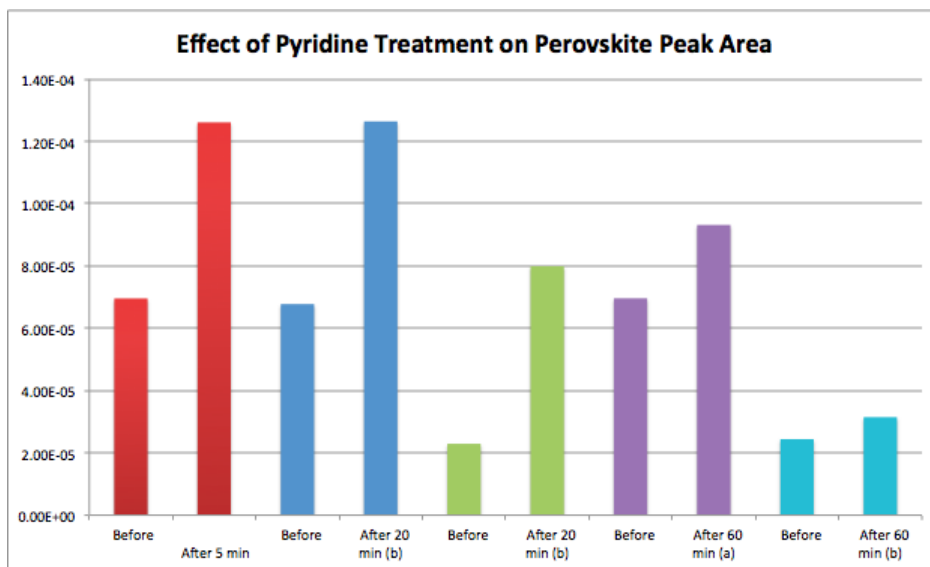

Figure 4a: Comparison of perovskite peak intensity before and after pyridine treatment for various samples.
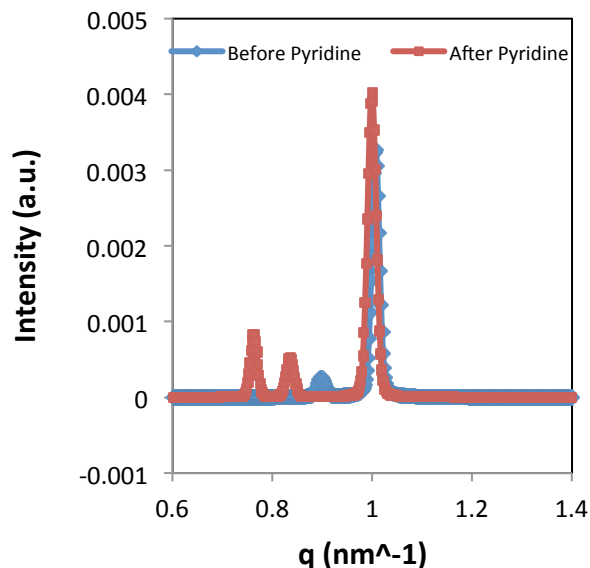
Figure 4b: Detail of 1D curves observed before pyridine treatment (blue) and after pyridine treatment (red) showing emergence of new peaks.

Figure 5 superimposes three plots: the intensity of the unknown species; the ratio of the (110) perovskite peak intensity after to that before treatment; and the ratio of the TRPL lifetime after to that before treatment. Though there is significant scatter and only two samples have been tested under each condition, Figure 5 suggests an inverse correlation between the amount of unknown species and improvement in perovskite peak area. At the same time, there seems to be a correlation between amount of unknown species and ratio of TRPL lifetime after to before pyridine treatment. This suggests that the unknown substance may impact the perovskite's performance, and could account for why we do not see improvement in lifetime despite the presence of more perovskite. Overall, the results reveal a variety of trends that merit further investigation.
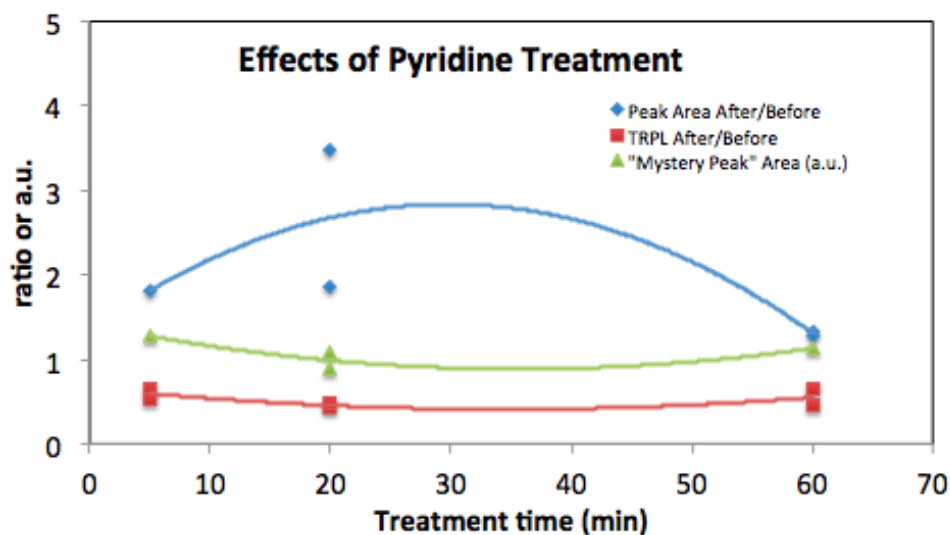

Figure 4: Correlations between intensity of mystery peak, improvement in perovskite peak area, and decrease in TRPL lifetime plotted against pyridine treatment time.

Conclusions

In an effort to improve the performance of perovskite films, the conditions for pure perovskite formation and the effect of pyridine vapor treatment were examined. We sought to test different annealing conditions to establish a standard procedure for high-quality perovskite formation. It was determined that annealing conditions of 100°C for 90 minutes followed by 120°C for 15 minutes was most effective. This recipe could be valuable for other researchers who want to study perovskites.

We were also able to build upon prior research on pyridine vapor treatment for perovskite films, and conclude that pyridine's effect on perovskite is more complex than originally thought. While it does seem to make the film more homogenous, it also has other effects: pyridine decreases overall PL lifetime, narrows the perovskite's bandgap, gives rise to a more intense perovskite peak, and results in introduction of an unknown species in the perovskite film. These results inform us about how pyridine interacts with perovskite materials, and provide an excellent starting point for more detailed study. In particular, the correlations observed between the intensity of the mystery substance, perovskite peak area increase, and decrease in TRPL lifetime should be investigated further. We hypothesize that understanding this species could ultimately give us the insight into post-processing solvent treatments necessary to take full advantage of their potential.

Acknowledgements

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