Effects of Polystyrene Coating on the Reflectance Spectra of Quasi-2D Hybrid Organic-Inorganic Perovskite Flakes

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***Abstract*—Quasi-2D Hybrid Organic-Inorganic Perovskite (HOIP) flakes possess reflectance spectra characterized by crests and peaks, called “modes”, that vary in their width and height. The reflectance spectra of these flakes are very sensitive to changes in their environment in the sense that these modes will shift in their wavelength position along the electromagnetic spectrum, and also change in their intensity, in response to different materials (with different optical constants) being deposited or coated on top of these flakes. The motivation behind us studying these HOIP flakes is that their reflectance spectra could serve as a sensor, because a change in intensity (change in brightness) or shift in wavelength (change in color) of the modes of these spectra could indicate to a human observer that some change in the environment has occurred. However, a major drawback that makes HOIP flakes tricky to implement in most real-world applications is that they rapidly degrade when exposed to oxygen. In the interest of both using these HOIP flakes as a sensor and preventing these HOIP flakes from degrading in oxygen, we spin-coated perovskite flakes with various thicknesses of polystyrene and analyzed how the reflectance spectra changed in response to these polystyrene coatings, and also over the course of many days following the polystyrene coatings. We find that polystyrene coatings induce additional cavity modes to these spectra and also successfully protect these flakes from degrading in oxygen when compared to a control sample that did not receive any polystyrene coating.**

***Index Terms*—Exciton, polariton, higher order mode, cavity mode, upper polariton branch, lower polariton branch.**

I. INTRODUCTION

Being able to quantify what certain changes in the environment cause what certain changes in the reflectance spectra of perovskite is necessary for its usage in sensor applications. The reflectance spectra of perovskite varies widely according to a variety of factors, though the reflectance spectra that we focused on studying exhibit three distinct features, being the higher order (HO) mode, lower polariton branch (LPB), and upper polariton branch (UPB) (see Figure 2). Our research is especially concerned with the changes in the HO mode, because it is the most narrow peak of all existing modes that may appear in a particular reflectance spectrum, which means very small changes in wavelength or intensity still result in large changes in intensity, at the original wavelength of the mode (as clarified in Figure 1).

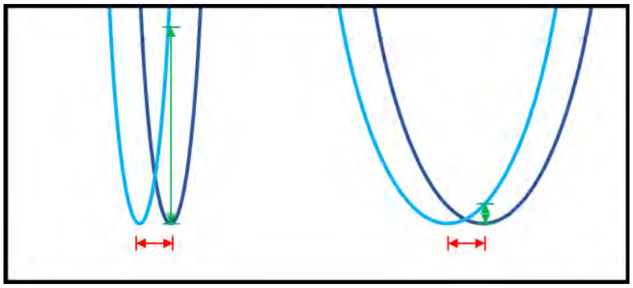

Figure 1. For the same shift in wavelength (red interval) from dark blue to light blue, the more narrow mode demonstrates much greater change in intensity (green interval) at its fixed, original wavelength, compared to the broader mode.

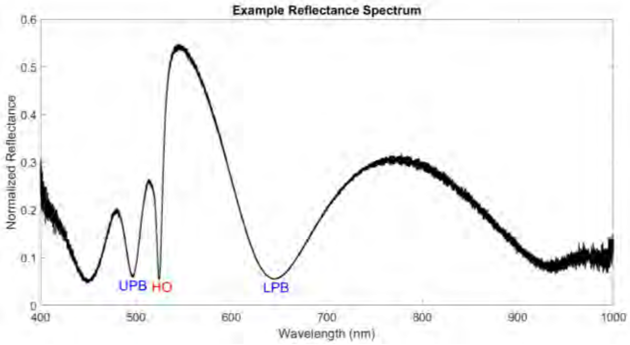

Figure 2. An example of an actual, experimental reflectance spectrum, with the various modes labelled.

(For clarification: we may sometimes describe modes and polariton branches with the word “peak” or “crest,” which suggest they point upward, though in the reflectance spectra, the modes point *downward*. However, the normalized *absorptance* spectrum would be the normalized reflectance spectrum minus the value one, so the modes would point upward in the absorptance spectrum be “peaks” by typical standards).

However, a major issue that makes perovskite impractical for implementation in real-world applications is the fact that it degrades in oxygen. This is one problem we wanted to address over the summer. Additionally, we saw instances where perovskite degrade rapidly when aluminum oxide is deposited on top of it.

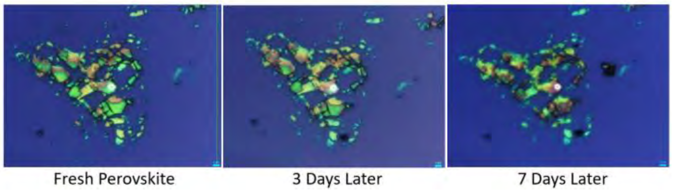

Figure 3. Perovskite degradation when exposed to air over time.

To address perovskite degradation issues, the main endeavor we undertook was to spin-coat perovskite flakes with various thicknesses of polystyrene and measure at regular intervals how the spectrum changes over the course of a week, as well as measure how the spectrum changes with respect to its original form. We therefore had two prongs of analysis with regards to the effects of applying polystyrene coating: perovskite preservation, and spectra changes.

II. BACKGROUND

A. History and Potential of Perovskite

While perovskite has been known to humankind for centuries—this naturally-occurring material was first discovered in 1839 by Gustav Rose in the Ural Mountains of Russia [1]—2D HOIP flakes have only recently been the subject of increased study in research labs across the world due to its potential for high power conversion efficiency (PCE), for usage in solar cells, and its demonstration of already being able to achieve relatively high PCE. While in 2009, the PCE of organic-inorganic metal halide perovskites were as low as approximately 3.8% [2], in a 2021 *Nature* publication, Yoo, J.J., Seo, G., Chua, M.R. *et al* reported a power conversion efficiency of a little over 25% [3], which is comparable to that of Silicon-based solar cells [4], and a particular chalcogenide perovskite/crystalline Si "tandem architecture" shows theoretical PCE exceeding 38% [5], which, currently, only multi-junction solar cells can achieve [4]. While our research is concerned with particularly the sensor applications of perovskite, we give this background to demonstrate why perovskite has been the subject of increased study and scrutiny in recent years.

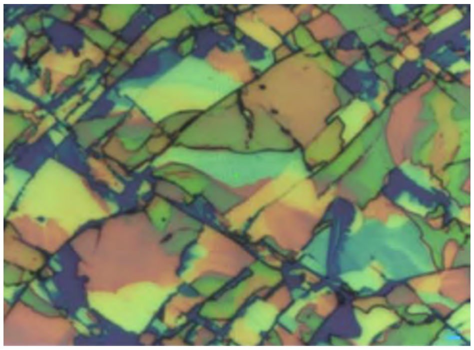

Figure 4. RP1 flakes on Si substrate under an optical microscope. The different colors of the flakes are due to the flakes being of different thicknesses (from most thick to least: green, red, yellow, blue).

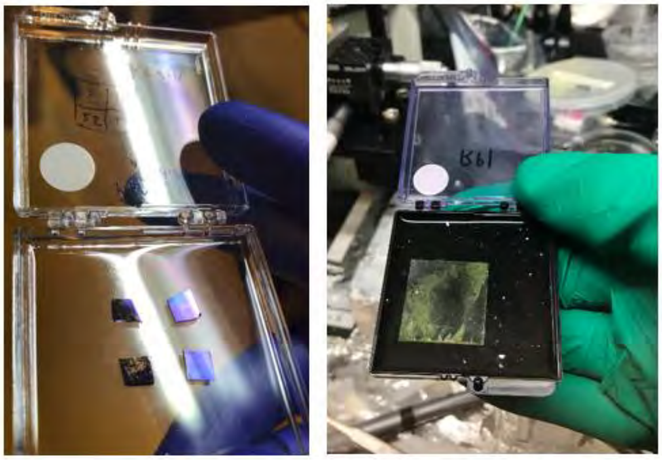

Figure 5. Perovskite flakes from a human eye's perspective, on squares/substrates from a 300nm SiO_2/Si wafer (left), and in large quantity on glass (right).

B. The Physics Behind the Modes

When the perovskite is encased inside a cavity (i.e. encased between the substrate and the material deposited on top of it), the top and bottom of the cavity act like parallel mirrors in the sense that a certain resonant frequency of light can oscillate back and forth inside the cavity, depending on the cavity's thickness (i.e. distance between the parallel top and bottom). This light creates an exciton, which is an electron-hole pair formed when photons excite an electron the bandgap from the valence band to conduction band, and this exciton at some point then recombines and emits light at the resonant frequency. The exciton continues to repeatedly recombine and emit light extremely quickly, and this exciton-light combination is together considered a particle called a "polariton," and is an example of light-matter coupling. When light and matter couple, there are hybrid states created that electrons can now inhabit, which, in the spectra, is seen as dips in its form, called the upper and lower polariton branches [6,7]. When we vary the thickness of perovskite flakes, substrate types, and thicknesses and types of materials deposited on top, different modes arise and disappear because of varying degrees of light-matter coupling (as all the materials involved have different refractive indices and extinction coefficients). Additionally, the upper polariton branch is called such, despite being at a lower wavelength, because wavelength and energy are reciprocally related by Planck's equation, $E = hc/\lambda$ (h being Planck's constant, c being the speed of light), and vice versa with the lower polariton branch being at higher wavelength.

III. MATERIALS AND METHODS

We neglect scattering of light in our experiments because we are concerned with the normal ("normal" as in perpendicular to the sample) incidence and reflection of light, so we thus can neglect scattering in the non-normal direction. Additionally, we neglect transmittance, since the wafer pieces/squares that the perovskite flakes are bonded onto are very thick ("very thick" in the context of the nano-scale) and light would thus not effectively transmit through it. Due to this simplification, the normalized absorptance and normalized reflectance sum to the value one. Otherwise, transmittance, scattering, absorptance, and reflectance sum to the value one.

The perovskite we use in our experiments is of the "Ruddlesden-Popper" structure, which consists of slabs of lead iodide, separated by organic ligands, in a stack—hence the characterization of "hybrid organic-inorganic." We use RP1 perovskite in all of our studies in this paper, meaning the slabs of lead iodide have only one layer of lead-iodide molecules, though if the number of layers were two or three, the perovskite would be classified as RP2 or RP3 [8].

Perovskite flakes can be exfoliated in great quantity due to their extremely small size, as their areas typically fall within a 3x3 µm to 30x30 µm area. Thus, exfoliation of perovskite even onto a small 0.5x0.5 cm substrate can yield thousands of flakes that all vary in thickness, making perovskite a plentiful and easy-to-prepare material, using a simple scotch-tape transfer process from fresh perovskite on glass, onto whatever substrate we choose.

In terms of methodology, the raw data for the reflectance spectra of the flakes were measured using the LabRAM HR Evolution Raman Spectrometer (made by Horiba), and the actual flakes, during measurements, were held in the Linkam THMS600 stage, which most importantly holds the perovskite in an oxygen-deprived vacuum to prevent degradation during sessions of measurement-taking. Both the spectrometer and stage are controlled with the LabSpec64 software. The raw data was then normalized with the reflectance spectra of a silver mirror, by dividing the raw data of the perovskite reflectance spectra with the spectra of silver (corresponding element-by-element division), with the normalized spectra being entirely between zero and one throughout the range of its intensity (vertical axis, which has no units after normalization).

While the reflectance spectrum changes for different thicknesses of perovskite, we consistently obtain spectra with our three modes of interest for our data and analysis because we are interested in the HO mode, especially. Flakes that are dark green with a dark border are of sufficient thickness such that these three modes arise. The substrate we use for all of our polystyrene studies is from wafers of 300nm of SiO_2 on Si.

Between measurements, the perovskite, if we wish to prevent exposure to oxygen and atmospheric conditions, can be held in the nitrogen-filled, oxygen-deprived and humidity-deprived glovebox. All samples of fresh perovskite on a substrate were prepared in said glovebox as well, for the initial measurements. However, for our polystyrene studies, we left the sample outside to be exposed to air and atmospheric temperature and pressure conditions. We also have a control sample that did not receive polystyrene coating and was also left outside similarly. Since we load up to four samples at once into the Linkam stage to measure from, and these four samples were stored in the same portable sample gel box, the control sample received the same treatment as the one with coating as consistently as possible (e.g would receive same exposure to air as we walked the four samples from the sample-preparation lab to the spectrometer measurement room between floors, and so on).

The spin coating was done using a rotating platform with a sticky area in the center, for placing the sample such that it does not fly off during the spinning. The spin coater has variable RPM and time-duration settings, though we always held the time-duration at sixty seconds and only changed the RPM, from 600 up to 3600, at intervals of 600. The polystyrene is a viscous liquid that we stir for five minutes before pipetting droplets onto the sample to cover it completely. We then immediately run the spin-coater. After spin-coating, the polystyrene hardens somewhat (polymerizes) and becomes more akin to laminated plastic, though it can still be scratched off.

Figure 6. Spin Coater. The sticky orange-brown tape in the center of the rotating platform is where the sample is placed before spin coating.

The aluminum oxide was deposited on top of the perovskite flakes using physical vapor deposition by a lab member in the cleanroom.

We also possess a transfer matrix modelling simulation that is able to predict in advance what the reflectance spectra of these flakes will look like, based off of parameters such as the perovskite thickness, substrate type, material deposited on top of the flakes—if any—and its thickness, perovskite classification (e.g. RP1, RP2), and the refractive index and extinction coefficients of all of the materials involved. This is useful because using atomic force microscopy tool particular to our lab to experimentally determine the flake thickness requires exposing the sample to air as we measure from it, which may cause it to degrade. We also use this simulation simply as a sanity check for our experimental results. Over the summer, lab members used ellipsometry to obtain the optical constants of polystyrene, using the same batch used in my preservation change in spectra studies, such that I could simulate its behavior.

IV. EXPERIMENTAL RESULTS

Initially, our goal this summer was to study how different thicknesses of alumina affect the spectra, without any goal of perovskite preservation. However, the PVD broke down very early on into our studies of alumina, which forced us to pivot into preservation studies with polystyrene, since it was known that perovskite degrades in oxygen. Despite this setback, the data we gathered on alumina both pre-breakdown and post-repair proved to be useful for comparison with polystyrene. After the PVD was repaired, we deposited 35nm of alumina on a sample of RP1 and saw that the alumina caused extremely rapid decay, and correspondingly, the reflectance spectrum showed rapid decay as well.

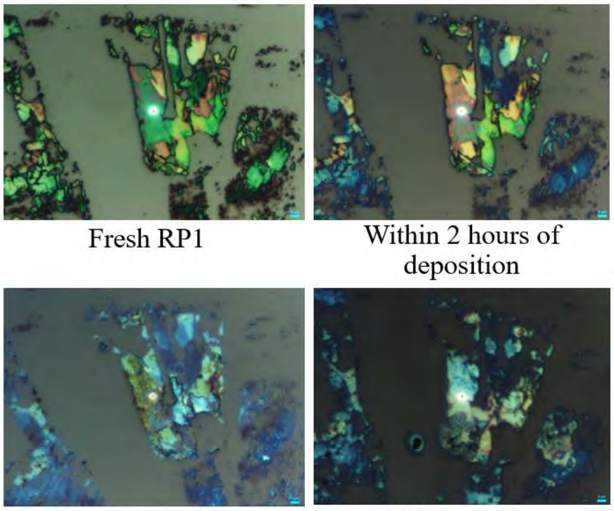
Fresh RP1
Within 2 hours of deposition
12 hours after deposition
32 hours after deposition

Figure 7. Pictures of the RP1 on Si substrate under the optical microscope of the spectrometer. The sample was left out to be exposed to air between measurements.

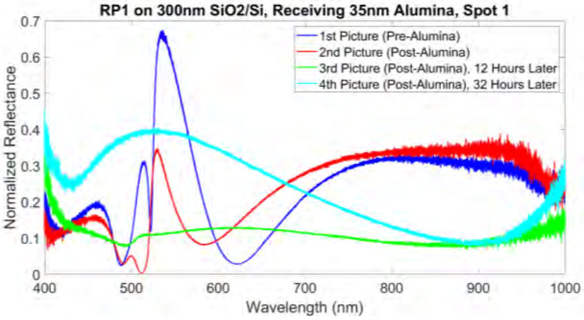

Figure 8. The reflectance spectra corresponding to the pictures shown above. We see that for the green and cyan plots corresponding to the bottom left and right pictures (heavy decay), the spectrum loses its modes.

In another sample that we 1) measured shortly after initial alumina deposition, 2) held in the glovebox for 42 days then measured from again, 3) left outside to be exposed to air and measured from again after one and three days, we did not see a very drastic degradation for several-day exposure to air, like we did for the above sample:

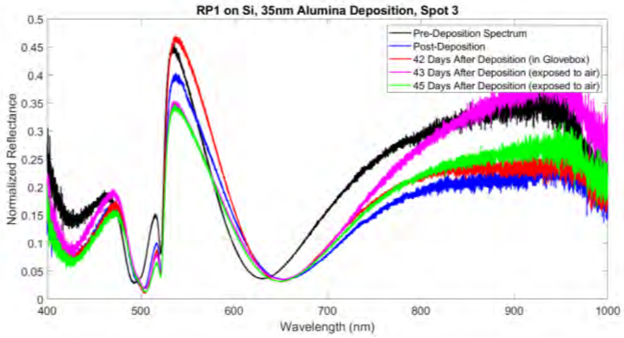

Figure 9. Reflectance spectra of the aforementioned sample. We see the spectrum remains intact, and under the microscope, the flake did not visually degrade (i.e. change color).

This data, compared to polystyrene's (which we will present shortly), suggest polystyrene is a more effective candidate in protecting perovskite because the alumina deposition was inconsistent in its ability to protect perovskite and in one case, seemed *harmful* to perovskite and quickly degraded it. However, polystyrene was consistent in its ability, at different thicknesses, to preserve perovskite over time. Additionally, polystyrene is theoretically a better candidate because, as initially a viscous liquid (before polymerizing/hardening), it conforms to the sides and top of the flake, while since PVD deposits alumina vertically on top of the sample, if we deposit a thickness of alumina less than that of the flake, the sides of the flake are not fully encased.

Thus, we decided to try different RPMs of polystyrene coating, specifically 600 to 3600 RPM at intervals of 600. The time-duration of the spin-coating we held at 60 seconds. Prior to all of the coatings, we chose flakes that gave reflectance spectra that have higher order modes, and the two polariton branches. We then measured these samples at regular intervals throughout the course of a week, leaving them outside of the glovebox to be exposed to air between measurements.

What follows are three reflectance spectra, for 600 RPM and 3600 RPM, and a control sample that did not receive any polystyrene coating, over time.

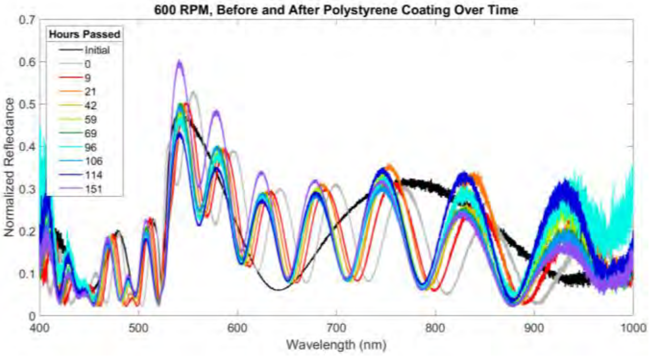

Figure 10. Reflectance spectrum over time, for 600 RPM.

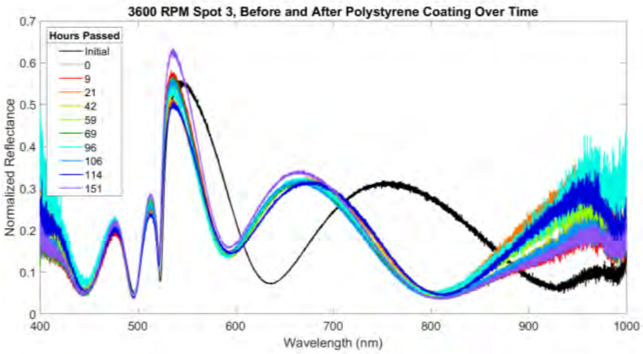

Figure 11. Reflectance spectrum over time, for 3600 RPM.

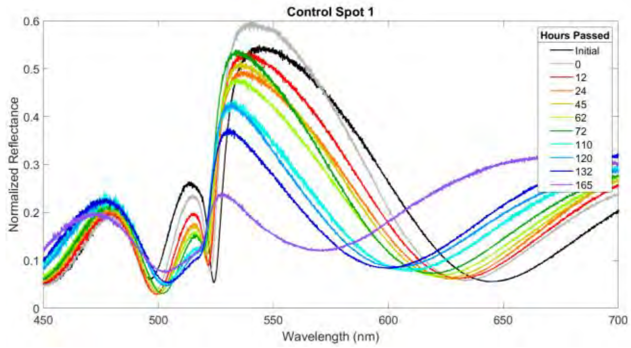

Figure 12. Reflectance spectrum for the control sample (we change the wavelength interval on the x-axis between 450 and 700 to give clearer, for better visualization on how the HO mode disappears).

We see that the spectra remain intact over the course of week left outside, for samples receiving coating (Figures 10 and 11), while the control sample decays (Figure 12). A particular point of interest is that the higher order mode is generally preserved for the samples with coating, though slightly shifted in wavelength or intensity.

We also see that for 600 RPM and thus the thickest of the coatings we applied, there were a great deal many cavity modes introduced, due to thin-film interference. In contrast, for 3600 RPM and thinnest of the coatings we applied, there were not nearly as many cavity modes introduced.

To help emphasize this point, we present a plot of one of each of the reflectance spectra for the different RPMs we chose, stacked:

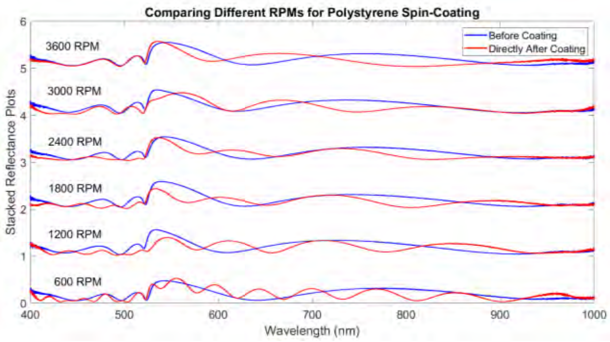

Figure 13. Stacked reflectance spectra, one from each of the RPMs. The reflectance spectra look stretched-out due to the different axes scaling. We see the number of cavity modes decreases as the coating becomes more thin. Additionally, thinner coating seems to induce less change with respect to the original spectrum, in general.

We then fit the simulation with our data in order to estimate the thickness of the polystyrene coating for each RPM.

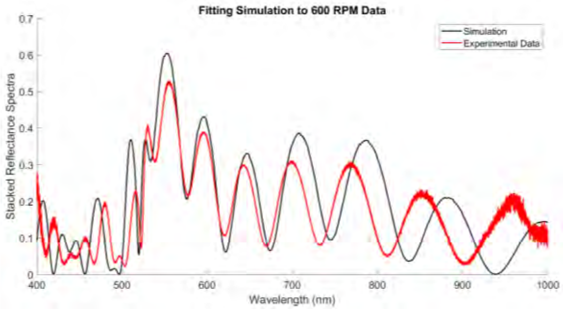

Figure 14. An example of fitting the simulation to the experimental data, for 600 RPM.

RPM	Sim-Suggested Polystyrene Thickness (nm)
600	~1815
1200	~900 to 975
1800	~700
2400	~500 to 600
3000	~550
3600	~415 to 525

Figure 15. Suggested polystyrene thicknesses for each RPM.

As a sanity-check, we also see in the following plots from the simulation that both that the HO is maintained for all coating thicknesses, and that cavity modes are introduced, the number of which is dependent on the polystyrene thickness. We also see that the simulation suggests that the thickness of the coating decreases with higher RPM. We can thus confirm our experimental data and our expectation of changing thickness with RPM is reasonable.

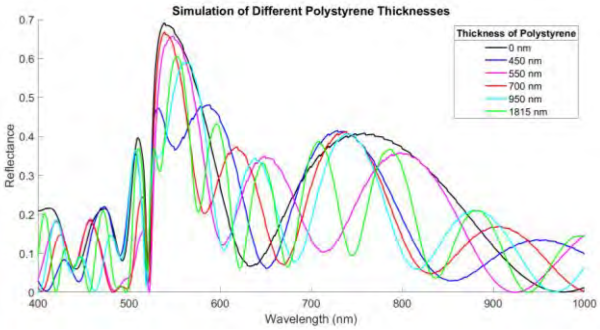

Figure 16: Simulation of the effects of the different thicknesses of polystyrene coating.

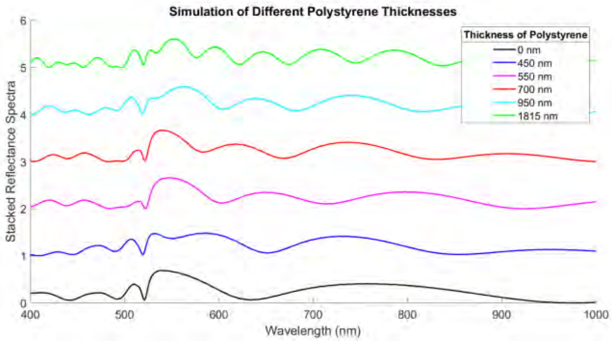

Figure 17. The previous figure, except stacked for greater visual clarity.

From here, we now delve into a more in-depth analysis. The plots that follow show the changes in intensity of the spectra over time, with respect to the initial intensity (all along the imaginary vertical line at the original wavelength of the mode, as demonstrated earlier in Figure 1), for the HO Mode, LPB, and UPB. We also present a math equation to clarify how these data points were calculated.

$$\text{For fixed } Wavelength_{initial} : Intensity(t) - Intensity(initial) \text{ for } t \geq 0,$$
$$t \text{ being time since polystyrene coating applied.}$$

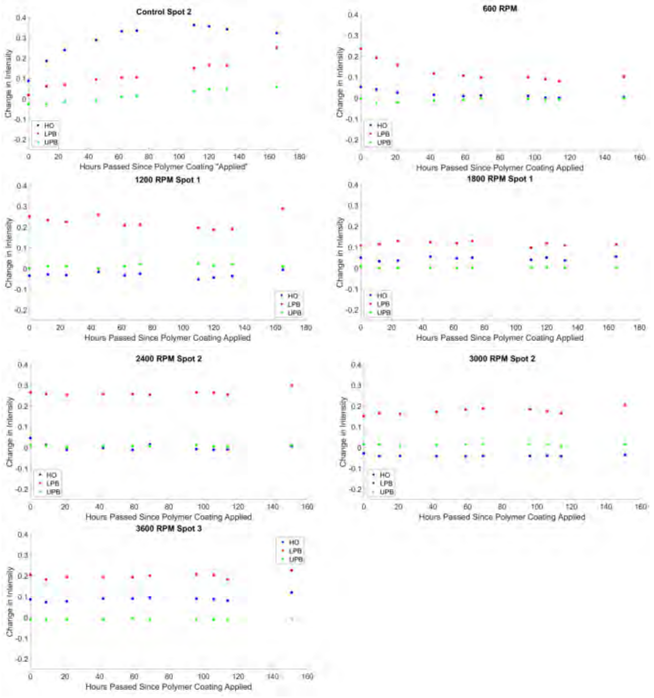

Figure 18. Plots of the change in intensity with respect to the initial intensity, for the three modes.

We see from the plots that for the samples with polystyrene, change in intensity with respect to the original intensity for the three modes remain relatively flat for the HO mode, LPB, and UPB, and especially flat as the coating is thinner. This is in contrast to the control sample, where the data points curve upward (the other control flakes showed similar curve), meaning the change in intensity is changing with time fairly drastically. Additionally, we see that when the polystyrene coating is applied, the LPB shows the most change in intensity with respect to its original intensity, for all of the RPMs. This is explained by the fact that the polystyrene, for all of our RPMs, introduces a cavity mode where the LPB was before, such that there is a large change in intensity compared to the other modes.

Additionally, we now present the *percent* change between points, which were created using the change in intensity plots we discuss in the last paragraph, and which we calculated because percent change between data points is another way to visualize change over time, and arguably a more effective way to visualize it. We calculated percent change between points using the standard percent change formula, in this case:

$$\frac{Intensity(t_n) - Intensity(t_{n-1})}{Intensity(t_{n-1})} \times 100$$

We present the plots below.

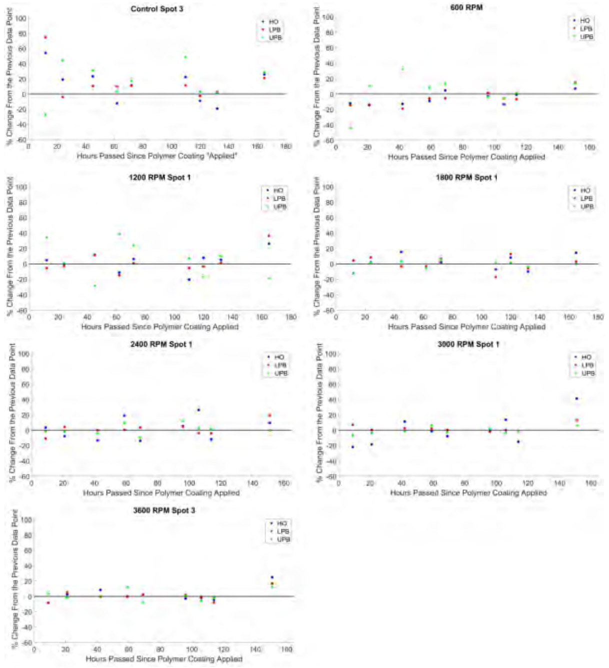

Figure 19. Plots of percent change, one from each RPM, for the HO Mode, LPB, and UPB. There is a horizontal black line drawn at zero, for better visualization of the data.

We see that for the percent change plots for the polystyrene coatings, the data points hover closer to the zero-line than the control, meaning there is not much percent change from point-to-pont over time. Additionally, at higher RPMs (thinner coatings), the points generally stay closer to the zero-line than for the lower RPMs. These percent change in intensity plots confirm the conclusions we drew during our initial analysis of the raw change in intensity plots.

V. DISCUSSION AND CONCLUSION

From our results throughout the summer, the first conclusion we can draw is that for higher thicknesses of polystyrene, there is a greater number of cavity modes introduced to the spectrum. For this reason, a future avenue of study that would be valuable to pursue would be to determine the most thin, non-invasive coating of polystyrene that one can coat onto perovskite, that both perturbs the spectrum the *least*, and still can protect it from degradation in oxygen.

One future application of these results is that if there is a spectrum from perovskite that we want to capture or eternalize for any reason, having a very thin, non-invasive layer of polystyrene could accomplish this.

To demonstrate another promising future application of these results, as a finalizing experiment, we decided to coat perovskite with a thin polystyrene coating (at 3600 RPM), measure from it, then deposit 5nm of alumina on top, then measure from it again. The following plot shows the spectrum after the introduction of each layer of material:

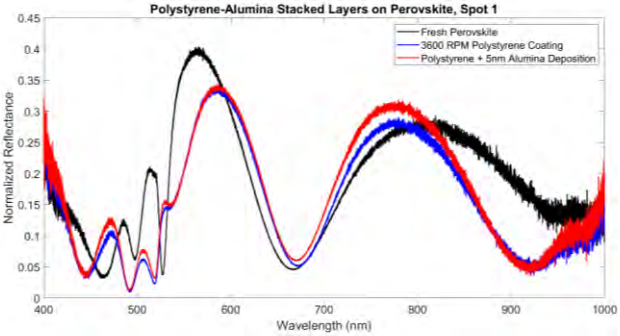

Figure 20. Reflectance spectrum and how it changes after the introduction of each material.

The purpose of this finalizing experiment is as a proof of concept; to show the feasibility of first coating polystyrene on perovskite, then layering another material on top of that polystyrene, and still having the reflectance spectra maintain relatively clear modes by the end for use in a sensor application. We see the polystyrene perturbs the spectrum slightly, and then the alumina deposition perturbs again (the polystyrene used in this finalizing experiment was from a freshly-made batch, which may explain why it shifts the HO mode and does not introduce a cavity mode, as the previous batch did. We suspect there was some difference in the preparation of this new batch compared to the last one. But we evaluate this experiment at a high-level, in terms of an overall proof-of-concept). This approach could in the future be used to allow people to introduce the effects of materials that would be harmful to perovskite to its spectra, while preventing this harmful material from actually degrading the perovskite due to the thin, non-invasive polystyrene "shielding" in between.

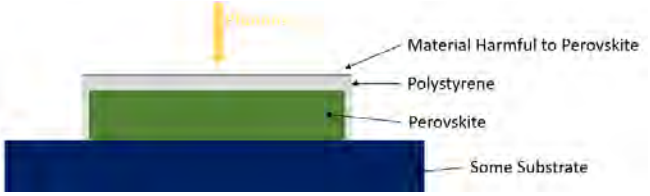

Figure 21. Schematic of why polystyrene may prove useful, if wanting to use material harmful to perovskite in conjunction with perovskite.

Perhaps, polystyrene (or other polymer) could even be used to separate multiple layers of material deposited on top of perovskite, such that people could introduce the effects of many different materials in stages—and thus change the spectrum in stages—therefore granting even greater freedom and control over manipulation of perovskite's reflectance spectra.

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