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Instability in perovskite solar cells is the main challenge for the commercialization of this solar technology. Here, a contactless, nondestructive approach is reported to study degradation across perovskite and perovskite/silicon tandem solar cells. The technique employs spectrally and spatially resolved absorptivity at sub-bandgap wavelengths of perovskite materials, extracted from their luminescence spectra. Parasitic absorption in other layers, carrier diffusion, and photon smearing phenomena are all demonstrated to have negligible effects on the extracted absorptivity. The absorptivity is demonstrated to reflect real degradation in the perovskite film and is much more robust and sensitive than its luminescence spectral peak position, representing its optical bandgap, and intensity. The technique is applied to study various common factors which induce and accelerate degradation in perovskite solar cells including air and heat exposure and light soaking. Finally, the technique is employed to extract the individual absorptivity component from the perovskite layer in a monolithic perovskite/silicon tandem structure. The results demonstrate the value of this approach for monitoring degradation mechanisms in perovskite and perovskite/silicon tandem cells at early stages of degradation and various fabrication stages.

1. Introduction

Over the past decade, perovskite solar cells (PSCs) have advanced rapidly in device efficiencies with significant opportunities for a low-cost, industry-scalable photovoltaic (PV) technology. Single-junction PSCs have reached a light-to-electricity conversion efficiency of 25.2%. Concurrently, perovskite/silicon tandem structures are attracting significant attention from the PV community as one of the most promising pathways to overcome the fundamental limit of single-junction solar cells. Monolithic perovskite/silicon tandem cells have achieved a record efficiency of 28% which is higher than that of crystalline silicon (c-Si) solar cells.[1] However, a major challenge for PSCs is their sensitivity to the surrounding environment and operating conditions. Light, oxygen, temperature, humidity, electric field, and more can all induce degradation in PSCs.[2–6] Therefore, an insightful understanding of the degradation mechanisms of PSCs is critical for the development of stable perovskite and perovskite/silicon tandem solar cells.

The most direct way to observe degradation is to monitor finished solar cell performance through standard PV parameters including external/internal quantum yields, short circuit currents, open circuit voltages, fill factors, and efficiencies.[7–10] However, these are global parameters and thus cannot give information about how different degradation mechanisms evolve across the solar cells. Also, this approach requires a complete cell structure. Another common approach is to monitor photoluminescence (PL) or electroluminescence (EL) intensities of the devices via both mapping and imaging tools.[11–15] This approach yields spatial information and does not require a complete device (in case of PL measurements). However, luminescence intensity can be confounded by several competing mechanisms. Under excitation, there are two phenomena simultaneously happening and affecting the luminescence intensity—ion migration and light-induced trap deactivation.[16–19] The response rate to each phenomenon varies depending on initial qualities of the samples and also during the degradation process.[16–19] These two phenomena often obscure the detected luminescence signal during the intended degradation tests.
especially at their early stages. Meanwhile, the material composition, thus the optical bandgap and absorptivity, is not affected by the two phenomena. Therefore, it is desirable to have a contactless, non-destructive method which can reliably monitor real spatially resolved degradations of perovskite and perovskite/silicon tandem solar cells at various fabrication stages.

In this work, we present an approach to study degradation processes in perovskite and perovskite/silicon tandem solar cells via spatially and spectrally resolved absorptivity. The absorptivity is extracted from PL spectra and directly related to the generation of free electrons and holes inside perovskite films under light absorption. First, we explain the underlying physics of the technique. After that, we examine various mechanisms that could potentially influence the absorptivity extracted. We then apply the technique to study various factors causing degradation of PSCs and compare the results with other common techniques. Finally, we briefly demonstrate the benefits of the technique to study degradation of monolithic perovskite/silicon tandem solar cells.

2. Method Description

First, we explain the method of extracting the absorptivity from PL spectra. The spontaneous generation rate of photons from each volume element of a semiconductor under excitation is given by the generalized Planck law:[20–24]

$$d\rho_{\nu}(\hbar \omega) = C \times (\hbar \omega)^3 \times \alpha \times \exp\left(-\frac{\hbar \omega}{kT}\right) \times \exp\left(\frac{\Delta \mu}{kT}\right) \times d\hbar \omega \quad (1)$$

$\alpha$ is the absorption coefficient of the emitting material and wavelength dependent. $k$ is Boltzmann’s constant and $T$ is the absolute temperature of the sample. $C$ is a physical constant. $\Delta \mu$ is the quasi-Fermi splitting between electrons and holes under illumination. $\Delta \mu$ is wavelength independent and thus the term $\exp(\Delta \mu/kT)$ is also a constant at a given injection level and temperature. Once generated, these photons can be reabsorbed when moving toward the sample surfaces. At the surfaces, some photons are reflected whereas some can escape out of the sample. To obtain the total photon flux outside the sample, one has to integrate Equation (1) over its thickness and account for the reabsorption of the spontaneous photons and surface optics. In general, the PL spectrum emitted from the sample is given by:[20–24]

$$PL(\hbar \omega) = C \times (\hbar \omega)^3 \times A \times \exp\left(-\frac{\hbar \omega}{kT}\right) \times \exp\left(\frac{\Delta \mu}{kT}\right) \quad (2)$$

$C$ again is another physical constant. $A$ is the absorptivity of the sample and wavelength dependent. It contains the absorption coefficient, sample thickness, and surface optics on both sides. An advantage of extracting $A$ from Equation (2) is that an absolute spectral intensity is not required. In principle, one can capture the PL spectrum in a relative unit and extract the relative A spectrum by dividing the PL signal by $(\hbar \omega)^3 \times \exp(-\hbar \omega/kT)$ according to Equation (2). A scaling factor (SF) can be obtained using absolute values of $A$ from spectrophotometer measurements at short wavelengths (i.e., high energies). Then, the entire relative A spectrum can be scaled to absolute A values. Note that, the scaling factor contains three parameters—the physical constant $C$, the detected fraction of the emitted spectrum, and the term $\exp(\Delta \mu/kT)$. The first two parameters are the same across the sample whereas the third parameter is location specific. Consequently, each location on the sample will have its own scaling factor.

However, for Equation (2) to be valid, there are several underlying assumptions. First, the spectral shapes are not affected by the excitation. Second, there is no parasitic emission from other layers in PSCs. Third, carrier diffusion and photon smearing do not affect the PL spectral shape detected. The two phenomena in the third assumption can cause heterogeneities in both excess carrier and emission profiles. The carrier diffusion happens when the excess carriers generated at the excited location move laterally in the sample and recombine. The photon smearing is due to the PL ray moving laterally in the sample and escaping it at a location different from the excited location. The third assumption is often valid for a macroscopic PL spectroscopy system in which the excitation area is larger than the detection area. In our micro-PL mapping system whose schematic is given in Figure 1a, the excitation spot size is a few micrometers in diameter and comparable with the detection area. Thus, it is critical to validate all three assumptions.

Figure 1b compares normalized PL spectra from a working PSC with various excitation powers whereas Figure 1c compares normalized EL spectra with various applied voltages. For PL measurements, the excitation power varies one order of magnitude. For EL measurements, a 100-mV difference in biased voltage corresponds to approximately a forty-fold difference in injection level. The PL spectra are all identical and so are the EL spectra, demonstrating that the excitation does not play a role in the luminescence spectral shape from our PSCs. Otherwise various injection levels would have varying degrees of impact on the luminescence spectral shape. In addition, the EL and PL spectral shapes are identical (Figure 1c), confirming no PL emission from other layers in the cell. Finally, for EL measurements, the excitation and emission profiles are uniform across the sample as the bias voltage is applied uniformly. Therefore, the third assumption of the negligible effects of the carrier diffusion and photon smearing on the shape of the detected PL spectrum is valid.

One critical parameter in Equation (2) is the absolute temperature. In fact, we can extract the actual temperature by fitting the slope of the high-energy side of the PL spectrum using the absorptivity measured by a spectrophotometer (see the Experimental Details for the spectrophotometer measurement procedure). The spectral-dependent absorptivity of photons at the high-energy side of the PL spectrum is high (>0.6) and thus spectrophotometer measurements still give highly accurate values. This is, indeed, a very well-established method employed by numerous authors to extract sample temperatures from luminescence spectra.[25–28] Figure 1d shows the fitting of the high-energy side with various temperatures. We found that a temperature of 315 K gave the best fit and was more realistic than room temperature as the sample could be locally heated under excitation. Many authors also reported the same observation.[25–28] Thus, in this study, we use the temperature of 315 K for all calculations.
3. Results and Analysis

In our PSC designs, light cannot transmit through the cells due to gold contacts on their rear side. A light ray passing through a cell hits the gold contact and is reflected back to the front side. The total absorptivity $A_{\text{total}}$ measured by the spectrophotometer is then equal to $1 - R_{\text{total}}$. At short wavelengths (<730 nm), parasitic absorption in the FTO/glass substrate is only $\approx 3\%$ (Figure S1, Supporting Information). Thus, the measured total reflectivity ($R_{\text{total}}$) at short wavelengths can be used to scale the relative $A$ values to absolute values.

Figure 2a,b show PL intensity maps of a PSC before and after a thermal degradation test at 90 °C for 30 min. Figure 2c shows $R_{\text{total}}$ at various locations before and after the degradation. The short-wavelength region (<730 nm) is identical among the locations. Thus, we can use $A_{\text{total}} \approx 1 - R_{\text{total}}$ at short wavelengths of the entire sample from spectrophotometer measurements to scale each relative $A$ spectrum (converted from the PL map) to an absolute $A$ spectrum for each pixel.

Now, we demonstrate the described method to extract spatially and spectrally-resolved absorptivity $A$ of a working PSC. Figure 3a shows a PL intensity map of the solar cell under an open-circuit condition. The cell structure and $I$–$V$ curve are given in Figure S2, Supporting Information. Each pixel (≈40 µm × 40 µm, determined by the scanning step size in both X and Y directions) contains an entire PL spectrum, allowing us to extract its $A$ spectrum by scaling to $1 - R_{\text{total}}$ values at short wavelengths. Figure 3b–d show extracted absolute $A$ maps of the cell at different wavelengths. Figure 3e compares the final $A$ spectrum extracted from the PL map (averaged over the 2 mm × 2 mm center of the solar cell) versus the $A_{\text{total}}$ spectrum measured by the spectrophotometer. The extracted $A$ spectra from various locations are given in Figure S3, Supporting Information. The scaling factor is determined from the average value of $1 - R_{\text{total}}$ between 690 and 700 nm. The two absorptivity spectra agree very well up to ≈770 nm (the optical bandgap of the material). They start deviating from each other at wavelengths longer than the optical bandgap. The spectrophotometer-based $A_{\text{total}}$ curve shows a saturated value $\approx 10$–20% at long wavelengths. This could be due to parasitic absorption or the reflected light scattered and trapped in the glass substrate, moving laterally and eventually escaping the integrating sphere. $^{[29]}$ On the other hand, the PL-based $A$ curve reduces to a few orders of magnitude below 1%. Note that the PL signal ≈780–850 nm is still a few orders of magnitude larger than the background noise (Figure 3e), yielding a small measurement uncertainty in this sub-bandgap wavelength region. Also, the parasitic absorption in the FTO/glass substrate is rather constant (≈3–5%, Figure S1, Supporting Information) across the wavelength range of interest. Consequently, the emitted PL spectral shape is not significantly affected by the re-absorption in the FTO/glass substrate.
Next, we apply the technique to study various degradation mechanisms of PSCs. Figure 4 shows evolutions of PL intensities, spectral peak locations (i.e., approximate optical band-gaps), scaling factors, and $A$ at various wavelengths from a PSC left at a room condition ($\approx 25^\circ\text{C, } 35\% \pm 15\%$ relative humidity). Their tabulated mean and standard deviation values are given in Table S1, Supporting Information. The PL intensity map (Figure 4, row 1) does not show a clear degradation over time. If we consider $A$ values at short wavelengths, for example, 740 nm (Figure 4, row 4), we cannot observe how the degradation evolves. However, at wavelengths longer than the spectral peak position, for example, 780–820 nm (Figure 4, row 5–7), $A$ values are $\approx 10\%$ or less and we can observe clearly the degradation process as an increase in $A$ with time. It is clear that the air slowly invades the cell through the edge of the gold contact. Also, we can observe various localized regions with different $A$ values in the cell, as indicated by the white circles in row 6 of Figure 4 ($A$ @ 800 nm). These features are not revealed clearly in the PL intensity map, for example, region A1 and A2.

Figure 5 compares the $A$ profiles across one of the localized spots (region A) and the edge region. Both profiles display an exponential decay of $A$ values versus distance from the cell edge or the center of region A. Based on these similarities, the localized spots must be affected by the air exposure over time due to pinholes on the gold contact as this is the only way the air can penetrate the locations without passing across the edge. Note that the solar cell was kept in a desiccator for a few days before we started the air exposure test. Thus, there could be an initial degradation around the edge even at zero hour (Figure 4, column a) due to the air present in the desiccator or during transit time between various labs. The region outside the gold pad also experiences the same air exposure-induced degradation with time. However, its initial $A$ value is different from that of the edge region inside the gold pad due to the different rear side optics.

In addition, Figure 6 compares the evolutions of PL intensities (6a), scaling factors (6b), $A$ values at sub-gap wavelengths (6c), and spectral peak locations (6d) with time. Correlations among these parameters are given in Figures S4 and S5, Supporting Information. The PL intensity (Figure 6a) shows different behaviors among locations and has different trends compared to the sub-gap $A$ (Figure 6c) and spectral peak location (Figure 6d). The PL intensity is determined by several mechanisms—light-induced trap deactivation, ion migration under light excitation, and actual degradation due to air exposure. Depending on the material and device quality at each location, its response rate to each mechanism varies. Thus, location A (affected by air exposure initially) and location B (representative for areas unaffected by air exposure initially) have different PL intensity trends (Figure 6a). Under the light-induced trap deactivation and ion migration, the PL intensity is altered whereas the PL spectral shape is identical. Thus, the spectral peak location and $A$ are not affected. However, under the air exposure, the material degrades and its PL spectrum shows a red shift and a reduction in intensity (see Figure S6, Supporting Information, for the data on bare perovskite films).
Thus, both the peak location and \( A \) show monotonic trends for all locations (Figure 6d,c). Although they give the same observation, analyzing \( A \) has its advantages compared to the former. The change of the peak location is very subtle (a few meV or nm at most) whereas that of \( A \) is significant, especially at sub-bandgap wavelengths. Therefore, small changes in the cell can be observed more easily and accurately using \( A \), especially at an early stage of degradation.

However, PL intensities, \( A \) values at sub-gap wavelengths, and spectral peak locations should be combined to gain more insights into the degradation process, in practice. The PL intensity is determined by both the quasi-Fermi level splitting under excitation, embedded in the scaling factor SF, and \( A \) values. Therefore, in principle there should be correlations between these parameters (PL, SF, and \( A \)). Indeed, the scaling factor strongly relates to the PL intensity as they both directly represent the number of photo-excited free carriers, as confirmed by their similar trends with time at different locations (Figure 6a,b). Their correlation factor is always very strong during the degradation process (>0.9, Figure S4b, Supporting

Figure 4. PL intensity, spectral peak location, and extracted \( A \) maps of a PSC versus exposure time in a room atmospheric environment (25 °C, 35% ± 15% relative humidity). Column a–f correspond to different exposure times. The first row (1) is the PL intensity map. The second row (2) is the spectral peak location map. The third row (3) is the scaling factor SF map. The next 4 rows (4–7) are the extracted \( A \) maps at different wavelengths. In row 6, the white circles denote the localized features discussed in the manuscript.
Information). Meanwhile, the PL intensity and $A$ also show a moderate relationship, but their correlation factor varies with time (Figures S4a and S5, Supporting Information), which is explained as follows.

In Figure 6, for locations initially affected by the air exposure (region A, blue curves), their $A$ values (6c) and spectral peak locations (6d) sharply increase in the first 10 h and their corresponding PL intensities (6a) sharply reduce. This corresponds to defect creations and hence a decrease of the quasi-Fermi level splitting due to the degradation (6b). After that (10+ h), their $A$ values and peak locations saturate, suggesting a nearly complete degradation process. Therefore, the light-induced trap deactivation and ion migration under excitation are likely to cause the increase of the PL signal. For locations far from the edge and initially unaffected by the air (region B, orange curves), their PL intensities slightly increase in the first 5 h whereas both the peak locations and $A$ values do not change yet, clearly indicating the excitation effects. After that (5+ h), the peak locations and $A$ values start increasing and the PL intensities start reducing, suggesting defect creations in the...
material due to the air exposure. As the degradation does not happen at the same time for locations across the PSC, the different effects of the excitation and degradation at different locations confound the relationship between the A values and PL intensities of the cell, leading to their moderate correlation factor (Figures S4a and S5, Supporting Information). We notice that when the degradation test is started, the material degradation happens and contributes to the PL intensity more and more significantly, yielding an increasing correlation factor A-PL with time (Figure S5, Supporting Information). However, once the degradation approaches the final stage, the correlation reduces and eventually becomes insignificant (Figure S5, Supporting Information).

Next, we continue investigating the evolution of PL intensities, spectral peak locations, and A values of PSCs before and after a thermal degradation test (90 °C, 1 h in a N₂ gas, Figure 7) and a light-soaking test (1-sun intensity, 30 min, no temperature control, Figure 8). Unlike the air exposure test, in the thermal test PL intensities reduce significantly and A values change uniformly across the entire cell (Figure 7). Also, A values at sub-bandgap wavelengths (e.g., 800 nm, Figure 7, row 3) reduce rather than increasing compared to the previous case. This seems to be consistent with the blue shift in the PL emission, suggesting a shift in the band edge. Meanwhile, in the light-soaking test PL intensities increase significantly and we can observe phase segregation effects via localized features (Figure 8, row 1).[12] Also, sub-bandgap wavelength A values increase for the entire solar cell, but various locations have varying degrees of increment (Figure 8, row 3). However, the spectral peak location map (Figure 8, row 4) does not show a clear pattern due to the very subtle bandgap variation across the cell. Note that these PSCs were kept in a desiccator for a few days before the degradation tests. Therefore, they could have been affected by the air exposure as can be seen by the increased A values at 800 nm around the edge (Figure 7a, row 3).

Figure 7. PL intensity, A, and spectral peak location maps of a PSC a) before and b) after the thermal degradation test at 90 °C for 1 h in a N₂ environment.

Figure 8. PL intensity, A, and spectral peak location maps of a PSC a) before and b) after the light-soaking test at 1-sun intensity for 30 min without temperature control. The temperature reaches ≈40–45 °C during the test.
Table 1 summarizes the changes in PL intensity, spectral peak location, and $A$ at sub-bandgap wavelengths after various degradation tests. Although the $A$ values and PL intensities can increase after a certain test (e.g., air exposure and light soaking for $A$ and only light soaking for PL), the performance of all PSCs reduces dramatically after all tests (air, heat, and light soaking) (Figures S7–S9, Supporting Information). Therefore, neither the PL intensity nor $A$ is a clear indicator of the device performance as they reflect mainly the absorber itself. The final device performance is a holistic reflection of various components including the absorber, transport layers, and contacts. However, monitoring $A$ values at sub-bandgap wavelengths is valuable for studying degradation mechanisms of various PSCs due to their high sensitivity. Generally, for a cell with reasonably low sheet resistance, the PL intensity map would not be expected to show significant variation since the two conducting planes at the top and bottom of the cell always keep the potential across the cell constant. Hence, PL intensity can be very difficult to use to study degradation on cells. When a significant variation in PL intensity does appear, it likely indicates a de-coupling between the potential at the contacts and the internal voltage or a composition change (e.g., phase segregation). $A$ values should be varied little with the former but significantly with the latter.

Beside a stronger sensitivity than the spectrophotometer-based method, another advantage of the PL-based method is to separate $A$ values of perovskite and silicon cells in monolithic perovskite/silicon tandem solar cells. Figure 9a–c shows PL intensity and $A$ maps of a 4 mm $\times$ 4 mm central region from a 2 cm $\times$ 2 cm tandem cell under an open-circuit condition. We used spectrophotometer-based $A_{\text{total}}$ values between 700 and 710 nm to scale PL-based relative $A$ spectra as light in this wavelength region is mostly absorbed in the perovskite layer. As the cell is still fresh, both the PL intensity and $A$ are relatively uniform across it. However, one can observe horizontal straight patterns in both the PL intensity and $A$ maps. They are due to wire saw patterns on the silicon wafer surface created during the wafer slicing process, causing a different in reflectivity and thus light absorptivity of the perovskite layer. An important point here is that the long-wavelength tail of the PL.

Table 1. Summary of changes in PL intensity, spectral peak location, and $A$ at sub-bandgap wavelengths after various degradation tests.

<table>
<thead>
<tr>
<th>Degradation Test</th>
<th>PL Intensity</th>
<th>Peak Location</th>
<th>$A$ at Sub-Bandgap</th>
<th>Patterns of Changes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air-exposure</td>
<td>Minimal variation</td>
<td>Slightly reduce</td>
<td>Significantly increase</td>
<td>Evolved from edges or pin holes</td>
</tr>
<tr>
<td>Light (1 sun, 30 min)</td>
<td>Significantly increase</td>
<td>Slightly reduce</td>
<td>Significantly increase</td>
<td>Localized, phase segregation</td>
</tr>
<tr>
<td>Heat (90 °C, 1h)</td>
<td>Significantly reduce</td>
<td>Slightly increase</td>
<td>Significantly reduce</td>
<td>Uniform</td>
</tr>
</tbody>
</table>

Figure 9. a) PL intensity and $A$ maps at b) 740 nm and c) 800 nm of a monolithic perovskite/silicon tandem solar cell. d) PL and $A$ spectra from the tandem cell. e) Various $A$ components from the cell.
spectrum emitted from the perovskite cell extends to ≈900 nm whose absorption depth in silicon is ≈30 μm.[32,33] The silicon solar cell is 150-μm thick, so the PL ray cannot pass through it and then be reflected back from the rear side. In this case, only reflectivities at the front surface of the tandem cell and at the perovskite/silicon boundary are important. We can treat the reflectivity at the perovskite/silicon boundary in a similar way to the case of the back reflectivity of the single-junction perovskite solar cells. Therefore, Equation (2) is still valid for tandem cells. If the PL ray passed through the silicon cell and then were reflected back from the rear side, the spectral shape would be affected by the silicon cell due to the varying absorption at different wavelengths in silicon.

Figure 9d shows average PL and A spectra obtained from the maps in Figure 9a–c, along with the A_total spectrum measured by the spectrophotometer. From the A spectrum of the perovskite layer and the A_total spectrum of the tandem structure, one can extract the remaining A spectrum of other layers (including the bottom silicon solar cell, interlayers, and top layers of the perovskite solar cell) (Figure 9e). We can see that around the optical bandgap of the perovskite material (700 nm), A of the perovskite layer is ≈40–50% and thus there is still a significant fraction of light absorbed in other layers. Combining the PL-based and spectrophotometer-based methods, we can separate the absorption inside the perovskite film from the entire tandem structure around the perovskite optical bandgap, which is otherwise impossible with the conventional spectrophotometer method alone. Although these results are preliminary, they demonstrate the high value of the technique to study degradation in tandem cells (mainly happen in the perovskite cell) by monitoring the absorptivity at sub-bandgap wavelengths of the perovskite film.

4. Conclusion
We have presented a method to map spectrally resolved absorptivity of perovskite solar cells using photoluminescence spectroscopy. Carrier diffusion and photon smearing are demonstrated to have negligible effects on the absorptivity extracted. Also, the results are not affected by parasitic absorption from other layers as they do not emit photoluminescence signals. The technique allows determining extremely small values of light absorption at the sub-bandgap wavelength region in which common spectrophotometer tools are not sensitive enough. We have demonstrated applications of the technique to study various common factors affecting degradation including room air and heat exposures and light soaking. The photoluminescence intensity measured is confounded by several mechanisms during the degradation tests whereas the absorptivity value reflects actual changes in perovskite material compositions. Also, the absorptivity at the sub-bandgap wavelength region is far more sensitive to the degradation than the material optical bandgap and thus can be employed to track the degradation in early stages. Another application of the technique is that it allows differentiating the absorptivity in the perovskite layer from the silicon and other layers in a perovskite/silicon tandem solar cell. This could be a powerful tool for studying tandem cell degradation mechanisms, which are mainly due to the unstable perovskite top cell.

5. Experimental Section

Perovskite Device Fabrication: A 70-nm thick TiO₂ compact layer was deposited on cleaned FTO/glass substrates by spin coating the titanium(IV) isopropoxide (97%, Sigma Aldrich) solution in 2-propanol with a spin speed of 5000 rpm for 15 s with a ramp rate of 5000 rpm s⁻¹. The compact TiO₂ film was then annealed at 500 °C for 30 min in a manual furnace. Afterward, a 100 nm-thick mesoporous TiO₂ layer was deposited on the substrate by spin-coating the 30 NR-D titania paste (Greatcell Solar) solution in ethanol (1:12 weight ratio) at a spin speed of 5000 rpm for 15 s with a ramp rate of 5000 rpm s⁻¹. The samples were then annealed at 500 °C for 30 min in the furnace. Once the substrates were cooled down to room temperature, a thin PMMA:PCBM passivation layer was deposited on the substrates at a spin rate of 4000 rpm for 15 s with a ramp rate of 4000 rpm s⁻¹. Detailed description regarding the preparation of PMMA:PCBM passivation solution can be found at ref. [34]. The dual-cation FA₃AₓCₓSₓ⁰ₙₓPe₁₁₃ₙ₉₃ₚ₉₃₌₃₉₃₅[FA: formamidinium] perovskite solution was prepared by mixing FAI (1.1 μl), PbI₂ (1.1 μl), CsBr (0.2 μl), and PbBr₂ (0.2 μl) in a solvent mixture of N,N-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) with a front/side ratio being 7:3. A two-step spin-coating process (1st step: 1000 rpm, 10 s, 100 rpm s⁻¹, 2nd step: 4000 rpm, 25 s, 1000 rpm s⁻¹) was used to coat the perovskite film on the substrates. After spin-coating, the samples were immediately transferred to a vacuum chamber and pumped down to low pressure (100–120 mTorr) for 10 s. The samples were then annealed at 100 °C for 30 min on a hotplate. Spiro-OMeTAD (LUMTEC) solution was prepared by dissolving 73.5 mg Spiro-OMeTAD in 1 mL chlorobenzene and the solution was doped with 17.5 μL of bis[trifluoromethane]sulfonimide lithium salt (Li-TFSI, Sigma Aldrich, 99.95% trace metal basis) (520 mg mL⁻¹ in acetonitrile) and 28.5 μL of 4-tert-butylpyridine (Sigma Aldrich, 98%). The spinning recipe for Spiro-OMeTAD 3000 rpm for 30 s with a ramp rate of 3000 rpm s⁻¹. Finally, an 80-nm gold layer was deposited on the Spiro-OMeTAD coated substrates using thermal evaporation. The active area of the cell (0.167 cm²) was defined using a shadow mask during the evaporation process. All depositions were conducted in a nitrogen-filled glovebox. A scanning electron microscopy image and I–V curve of a representative working cell are given in Figure S2, Supporting Information.

Monolithic Perovskite/Silicon Tandem Fabrication: The bottom c-Si sub cell was fabricated using an n-type 1–5 Ohm.cm wafer. The rear side was boron doped and passivated by an Al₂O₃/SiN₃ stack. The front side was covered by a layer of phosphorous doped poly-Si. The recombination layer between both sub cells was formed by a thin layer of ITO. The top perovskite sub cell was finished by NiO₃ through sputtering, perovskite, PCBM and AZO layer through solution process, and IZO though sputtering. The top metal grid was finished with gold thermal evaporation through a shadow mask.

Micro-Photoluminescence and Electroluminescence Spectroscopy: The system employed in this study was a Horiba LabRAM system equipped with confocal optics, a silicon charge-coupled-device (CCD) detector, and an automatic X-Y mapping stage. For PL, the investigated samples were excited with a continuous-wave diode-pumped solid-state (DPSS) 532-nm laser diode. The laser light was focused into the sample surface using a 10× objective lens with a numerical aperture of 0.25. The on-sample illumination spot size was ≈2.6 micron in diameter and the on-sample power was kept constant at ≈1 microwatt, corresponding to a power density of ≈20 W cm⁻². For EL, the samples were forward biased with voltages between 1–1.2 V. The spectra were all corrected for the spectral response of the entire system, determined by a calibrated halogen-tungsten light source. The scanning step size was 40 microns in both X and Y directions.

Spectrophotometers: Reflection and transmission responses of all samples were investigated using a PerkinElmer spectrophotometer equipped with both silicon and InGaAs detectors and an integrating sphere. The measurements were calibrated with a standard spectrolal. For reflection measurements, the light source was focused on the sample placed at the back of the integrating sphere via a lens. For transmission measurements, the sample was placed in front of
the entrance hole of the integrating sphere. The measurement spot size was ≈2 mm in diameter.

**Solar Simulator** I–V curves were measured using a xenon light source Photo Emission Tech SS150 solar simulator. Results were analyzed using an Autolab PGSTAT204 galvanostat/potentiostat. The samples were first light soaked for 10 s. After that, they were scanned from 1.2 to −0.05 V (reverse) and then immediately from −0.05 to 1.2 V (forward) both with a scan speed of 50 mV s⁻¹. No mask was used and the active area of the cell was defined by the area of the gold contact (16.7 mm²).

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

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**Conflict of Interest**
The authors declare no conflict of interest.

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