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Perovskite escape room: Which photons leave the film, and which are trapped inside?

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Although halide perovskite materials hold great promise for optoelectronics, defect-assisted recombination still limits their efficiency. In the April issue of *Matter*, Fassl et al. present an open-source model for analyzing the photoluminescence spectra of perovskite films, showing a much lower internal quantum efficiency than previously thought in the field.

Solar cells employing halide perovskite semiconductors as light absorbers have been rapidly developed, resulting in record power conversion efficiencies larger than 25%.[1] Combining these perovskite solar cells with commercial silicon solar cells into tandem cells has even led to record efficiencies of more than 29%. Additionally, halide perovskites have been successfully used as photoactive materials in other applications such as light-emitting diodes and radiation detectors, as well as in photocatalysis.[2,3] The excellent performance of halide perovskites in these applications is mainly due to the fact that the densities of detrimental defects are relatively low (~10^{15} cm^{-3}).[4] As a result of these low defect densities, light-generated charges can be efficiently collected. Vice versa, injected charges efficiently emit photons because of the high yield of radiative recombination compared with non-radiative defect-assisted recombination. In order to reach the thermodynamic efficiency limit for the above-mentioned applications, it will be essential to eliminate all defect-assisted recombination pathways. Ideally, the photoluminescence quantum efficiency (QE) is unity at the relevant charge densities, meaning that every electron-hole pair can *only* recombine radiatively.

Consequently, photoluminescence measurements are widely used for assessing the quality of halide perovskite samples and studying the effect of the synthesis method, composition, or post-synthetic treatments. Although measuring the photoluminescence is experimentally one of the most straightforward characterization methods, interpretation of photoluminescence spectra and/or lifetimes is not that trivial and requires detailed analysis.[5] This is especially a concern when dealing with thin films, where a substantial part of the emitted photons will be internally reflected and hence not detected in a photoluminescence measurement. In halide perovskites, the chance that an emitted photon will leave the film (escape probability)[6] is typically quite low because the refractive index (n ~ 2.6) is relatively high with respect to air. The escape probability varies with the surface roughness[7] and can change when a passivating or charge-transport layer with a different refractive index is deposited on top of the perovskite. Variations in the escape probability lead to differences in the intensity and/or spectral shape of the externally measured photoluminescence. Therefore, in order to use photoluminescence measurements to fully understand how an experimental variable, such as the synthesis method, affects the defect-assisted recombination, it is crucial to understand whether it affects the escape probability.

In the April issue of *Matter*, Fassl et al. present a rigorous method to analyze the externally measured photoluminescence spectra of methylammonium lead iodide ($MAPbI_3$) perovskites.[8] Measuring the photoluminescence inside an integrating sphere enables the authors to detect photons emitted in all directions, in contrast to measuring the photoluminescence at a single spot or angle. An important observation is that the photoluminescence spectra collected inside an integrating sphere are much broader and more red shifted than spectra collected from a 6 μm spot. In addition, collecting all emitted photons by using an integrating sphere shows that the spectral shape depends on the film thickness. Although the spectra collected from the top are similar, the integrating sphere measurements show that 260-nm-thick films emit more low-energy photons than 80-nm-thick films. These observations are interpreted from the reabsorption of emitted photons, which occurs when the wavelength of an internally reflected photon overlaps the absorption spectrum of the perovskite (see Figure 1). Because low-energy photons have less overlap with the absorption spectrum, these will eventually have a higher chance of leaving the film than high-energy photons. Fassl et al. refer to these non-absorbed low-energy photons (that leave the perovskite film after several internal reflections) as scattered photons.[8] The emission spectrum of these scattered photons is red shifted with respect to directly emitted photons, which leads to an additional peak in the photoluminescence spectrum. Because the ratio between the two varies from sample to sample, they argue that this combination of scattered and directly emitted photons could explain the wide variation in photoluminescence spectra reported in the literature.

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https://doi.org/10.1016/j.chempr.2021.03.017

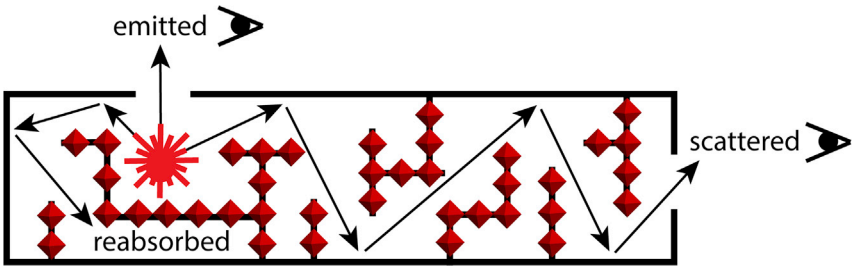

Figure 1. Schematic of the different pathways after a radiative recombination event in a thin perovskite film

The photons within the escape cone will be emitted externally (detectable), whereas the ones out of the escape cone will be reflected internally (not detectable). These internally reflected photons can be reabsorbed by the perovskite if their energy matches the absorption spectrum of the perovskite. Photons with lower energy are more likely to leave the film after several internal reflections (scattered; detectable in an integrating sphere).

Fassl et al. also present a fitting procedure to determine both the escape probability and the internal QE from the number of externally emitted photons per absorbed photon (the external QE). A high internal QE is associated with low defect densities and is therefore an important parameter for predicting material quality and device performance. Previous assumptions in the literature on the escape probability ranged from 5% to 13% and have led to estimated internal QEs of around 90%. However, Fassl et al. show that the escape probability is actually much higher and that consequently, the internal QE is more likely close to 80% (at ~10^{17} absorbed photons $cm^{-2}s^{-1}$). This means that the chance that a photogenerated electron-hole pair will recombine non-radiatively is approximately 20%: twice as large as previously estimated. Therefore, an important implication of this higher escape probability is that defect-assisted recombination in $MAPbI_3$ perovskites plays a larger role than what was thought before. In addition, the authors show how the internal reflection depends on both the wavelength of emitted photons and the film thickness, so that the internal QE cannot be obtained if one assumes a single value for the escape probability. Finally, $MAPbI_3$ on indium tin oxide (ITO) is used as a showcase for developing a fitting procedure that analyzes the parasitic absorption, i.e., the number of emitted photons that are reabsorbed by a contact layer. The authors predict that increasing the internal QE while minimizing the parasitic absorption will be necessary for solar cells to reach their thermodynamic efficiency limit because this will maximize the open-circuit voltage (V_{OC}).

The authors have provided the full curve-fitting model as an open-source MATLAB app, making it an easily accessible fitting procedure for others to analyze similar data without the need to reproduce the code. Although this initial work started with $MAPbI_3$ perovskites, the same approach can in fact be extended to any other thin-film semiconductor. Therefore, the article and freely available fitting procedure by Fassl et al. could find use in a much broader research community than those working on perovskite solar cells. Still, performing the full analysis might not be straightforward for everyone given that it still requires access to an integrating sphere. However, the observation that both the intensity and spectral shape of photoluminescence are very sensitive to the measurement conditions, as shown by Fassl et al., stresses the importance of carefully considering parameters such as surface roughness and film thickness when comparing photoluminescence spectra. In addition, one should take into account that contacting the perovskite with a passivating layer or charge-transport material could affect the photoluminescence intensity through changes in the escape probability and/or the parasitic absorption. Hence, although measuring the photoluminescence is relatively simple in comparison with other spectroscopic techniques, drawing conclusions on how an experimental variable affects parameters such as defect densities might require extensive data analysis or complementary measurement techniques.

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