OPTICAL SPECTROSCOPY

Picturing charge carrier diffusion

Spectral shifts in transient photoluminescence measurements performed with a confocal microscope allows tracking of charge carrier mobilities in polycrystalline halide perovskites.

Thomas Kirchartz[1,2]

Lead-halide perovskites have emerged as promising materials for photovoltaics as they tick several boxes needed for efficient solar cell materials. They absorb light efficiently and have very long charge carrier lifetimes, especially if compared to other polycrystalline materials.[1] Recombination at the surfaces and interfaces with contact materials is much less severe than in other photovoltaic technologies. However, the charge carrier transport in this material class is significantly worse than in many inorganic solar cell materials.[2] Charge carriers in efficient solar cells need to move from the point where they are created to one of the contacts within their lifetime. This process of charge extraction can be achieved by a combination of high mobilities and lifetimes of charge carriers in the absorber material, as well as the presence of two selective contacts, each of which allows either electrons or holes to leave the solar cell towards the outer circuit.[3] Solar cells work at substantial forward bias (the maximum power point), where a small or no electric field will aid the transport of charge carriers through the perovskite layer. Thus, the transport mechanism will be largely diffusive and given some previously reported diffusion coefficients and mobilities,[4, 5] one might wonder how lead-halide perovskites achieve such comparably high photovoltaic efficiencies and fill factors of up to 86%.[6]

Cho et al.[7] resolve this conundrum by determining vertical and lateral diffusion coefficients as a function of position within polycrystalline perovskite films using transient photoluminescence recorded with a confocal microscope. The decisive trick to determine vertical diffusion coefficients from PL transients lies in the use of spectral information as illustrated in Figure 1. Radiative recombination within a semiconductor will lead to a photon density whose spectral distribution is somewhat higher in photon energy than the spectral distribution of the detectable photon flux outside of the semiconductor. This discrepancy is the result of reabsorption, i.e. the semiconductor film partly illuminates itself, and the higher energy photons are more likely reabsorbed and therefore not detected than the lower energy photons. If a semiconductor is illuminated by a laser pulse of a certain wavelength (see Fig. 1a), more photons will be absorbed close to the front of the film than close to the back. This asymmetric distribution of charge carriers will create PL that has a higher average energy emitted at the earlier times than the PL at later times after photo-excitation, when diffusion has led to a more homogeneous carrier distribution throughout the film (see Fig. 1b). As diffusion controls the spectral shift (see Fig. 1c), the spectral shift can be used to determine diffusion coefficients or mobilities.[8] While this effect is generally known, its impact on spectral shifts in thin halide perovskite films has so far been largely ignored. By combining the concept of photon reabsorption with the ability to measure transient PL with a confocal microscope, Cho et al.[7] track diffusion coefficients in all three spatial dimensions as well as in time. The key finding is that the investigated polycrystalline formamidinium-lead-iodide films show spatially heterogeneous vertical diffusion with diffusion coefficients D varying by orders of magnitude from $D < 10^{-2}$ cm^2/s to $D \approx 1$ cm^2/s. For a significant fraction of the grains, transport is good enough to allow the electrons reaching the contacts within their lifetime solely by diffusion. The lateral diffusion coefficient ($D = 0.02$ cm^2/s) in the same sample is, however, consistent with the lower end of the vertical diffusion coefficients and agrees with earlier findings of poor charge transport in the literature.[5] This value is lower than needed for efficient collection and consistent with intragrain transport, i.e. the electrons pass grain boundaries during the lateral diffusion process.

The approach of Cho et al.[7] is also applicable to other emerging semiconductors and should become particularly useful for materials with anisotropic charge carrier or exciton diffusion. Cho et al.[7] further apply the method to two-dimensional halide perovskites where exciton diffusion is more efficient in the plane of the film than in the vertical direction. In the future, the approach may be extended to all semiconductors, with measurable emission intensity and sufficient spectral overlap between emission and absorption in order to leverage from the photon reabsorption to study diffusion. This may include absorber layers of organic solar cells, where charge carrier transport is a major impediment towards achieving higher efficiencies.[9]

Recently, steady-state photoluminescence measured at short circuit in halide perovskite solar cells has shown that the density of charge carriers, which stay in the absorber and cannot be collected, is surprisingly high.[10]. Currently, it is not clear whether the magnitude of this remnant charge carrier density is dominated either by poor charge transport in the absorber or in the electron and hole transport layers[3] that are often made of moderately conductive organic semiconductors. The method here could be used in the future to quantitatively compare the transport properties and elucidate the origin of poor charge transport to further optimise the performance of perovskite solar cells.

The authors declare no competing interests.

Affilliations
[1]IEK5-Photovoltaik, Forschungszentrum Jülich, 52425 Jülich, Germany
[2]Fac. of Engineering and CENIDE, Univ. of Duisburg-Essen, Carl-Benz-Str. 199, 47057 Duisburg, Germany
e-mail: t.kirchartz@fz-juelich.de

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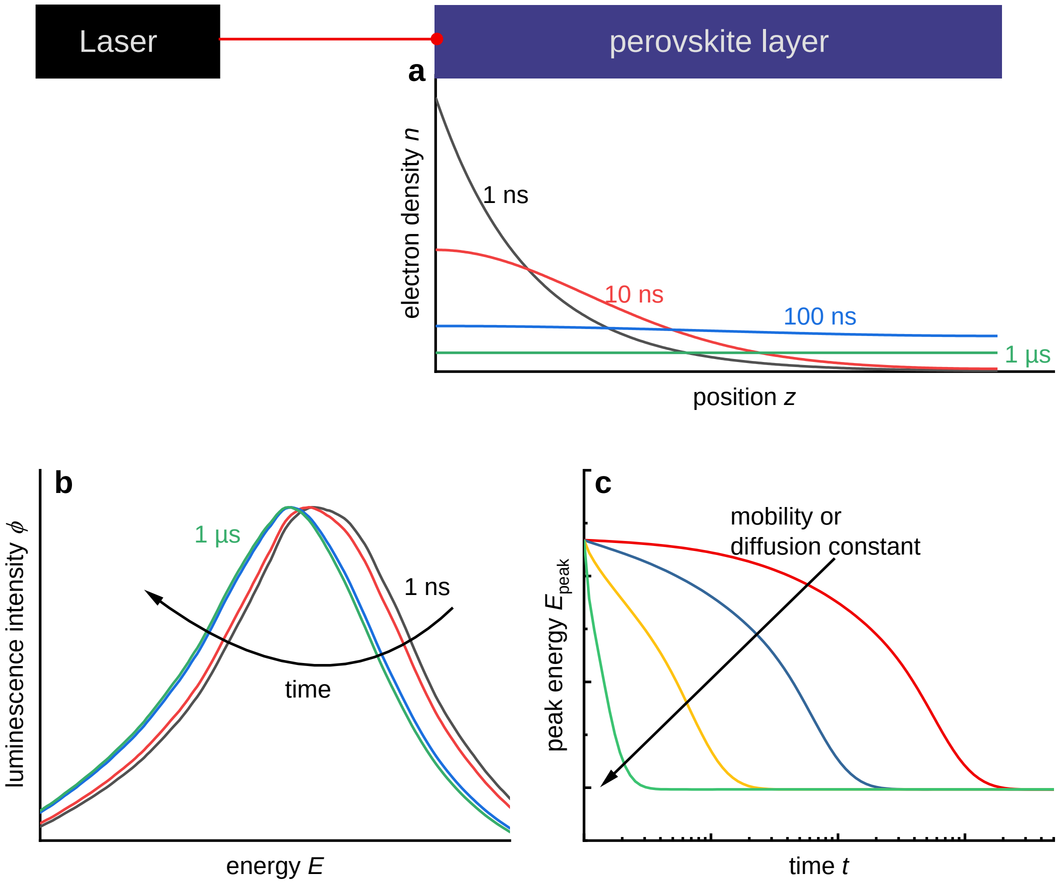

Figure 1 | Schematic illustration of the photon reabsorption effect. a As laser pulse hits the perovskite layer, electrons and holes are created whose density decays gradually from the front to the back of the film. Diffusion leads to a homogenization of the carrier concentration at later times after the pulse. **b** The observed PL spectrum shifts to lower energies as function of time as the amount of reabsorption of high energy photons increases when the electron density is more homogeneously distributed. **c** As the shift in the spectrum depends on the speed of diffusion, different diffusion coefficients or mobilities results in a difference in time taken for the shifts of the peak to take place that are then used to determine the diffusion coefficients.