Very long diffusion lengths in perovskite photovoltaic cells and other things

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Hybrid organic-inorganic perovskite photovoltaic cells have demonstrated rapid increase in performance over the past few years, but basic knowledge about why these materials have such good properties is lagging behind. One of the metrics of importance is the diffusion/drift lengths of the electrons and holes. Early on, values of a hundred nm (already a very respectable number for solution processed semiconductors), followed rapidly by 1-2 μm were reported. More recently, values up to several mm for single crystals have been reported.

Here we discuss the various factors that make these semiconductors so good for photovoltaic cells, finally zeroing in on the long lifetimes that necessarily lead to long diffusion lengths. Potential reasons for the long lifetimes (low deep trap densities; ferroelectric domain boundaries separating electron and hole pathways) are discussed.

At the same time, the very long diffusion/drift lengths that have been reported need to be treated with caution. Ignoring the difference between diffusion and drift for the moment. The (minimum) diffusion lengths reported for the perovskite single crystals were estimated from the fact that the photogenerated charges were able to move from one side of the crystal (up to 3 mm thick) to the other with small losses. The diffusion length of electrons or holes in a semiconductor is defined by the average distance the relevant charge moves in the semiconductor between generation and recombination/extraction from the semiconductor. According to this definition, these diffusion lengths indeed must be larger than the crystal thickness. However, such large diffusion lengths have been commonly seen in other semiconductors in the past, including in TiO_2 (which is not known for long electron diffusion lengths as normally defined). and in CdS or CdSe single crystal photoanodes. These examples will be described and it will be shown that the common factor between these examples and the perovskites is that one charge is removed rapidly (or in the case of TiO_2 in the dye cell, only one charge is injected into the TiO_2), leaving the other charge to move (mostly by diffusion since most of its trajectory to the other side of the semiconductor is in a field-free region).

When diffusion lengths are quantified, it is (or at least was) assumed that both charges are present in much of the semiconductor volume. Since some will compare a diffusion of 'millimetres' with a more common value of around a μm or less, it seems to be time for a more rigid definition of this important metric that separates between charge movement in an environment where both charges are present and one (as, e.g. in macroscopic single crystals) where almost all the relevant charge movement is in a region where the counter charge is absent. Of course, there will be cases (even commonly so) where charge movement takes place to a comparable extent both in the presence and the absence of counter charge: A good

example being a cell where the semiconductor thickness is more than a few times the absorption depth, but not very much more. However, it is hoped that some differentiation will allow a more meaningful comparison of diffusion/drift lengths between different cases.