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Perovskite Solar Cells

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Understanding the Outstanding Power Conversion Efficiency of Perovskite-Based Solar Cells

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Dedicated to Professor Fernando Langa on the occasion of his 60th birthday

perovskites · photovoltaic conversion · solar cells

Currently most solar cells are based on silicon and show efficiencies over 15%. Since the production of silicon-based solar panels is expensive, alternative technologies for energy conversion have evolved in the last decades based on organic materials (OPVs; organic photovoltaics) and hybrid materials (DSSCs; dye-sensitized solar cells). OPVs and DSSCs have the prospect of cheap large-scale production but still suffer lower power conversion efficiencies (8–13%).[1]

In the commercially available silicon solar cells, when a photon from the solar spectrum is absorbed, the exciton binding energy is so small that the electron and hole can separate, and thus a current can be produced. However, in an organic material, the absorption of a photon creates a strongly bound exciton, basically a neutral electron–hole pair. This means that absorbed photons produce a neutral excitation, not free carriers, and thus a dissociation interface is required. Within organic solar cells, for example, the well-known P3HT/PCBM heterojunction (Figure 1: Donor/Acceptor), the necessary steps to transform sunlight into electricity are: 1) absorption of sunlight and formation of the exciton; 2) exciton diffusion to the donor–acceptor interface; 3) exciton dissociation into free charges (electrons and holes), and 4) charge transport to and collection at the electrodes.[2]

In the past few years the photovoltaic field has experienced a dramatic boost due to the development of perovskite-based solar cells (PSCs). They have shown an unprecedented speed of evolution and outperform established organic and hybrid materials already after only few years of investigation. PSCs were initially introduced as type of DSSC, but subsequent studies indicated they have a unique working mechanism. Consequently, these so-called “third-generation solar cells” have been one of the hottest topics in sustainable energy science. However, since the first highly efficient devices were published, their working principle has been matter of debate.[3]

One of the first research papers dealing with this issue was written by Mora-Sero, Park et al.[4] They observed charge accumulation in the light-harvesting material $CH_3NH_3PbI_3$, thus indicating that perovskite solar cells indeed constitute a new kind of photovoltaic device. In a later report by Snaith, Petrozza et al.,[5] the exciton binding energy of the $CH_3NH_3PbI_{3-x}Cl_x$ perovskite crystal was estimated to be roughly 50 meV, which corresponds to almost full ionization under operating conditions similar to that in Si-based solar

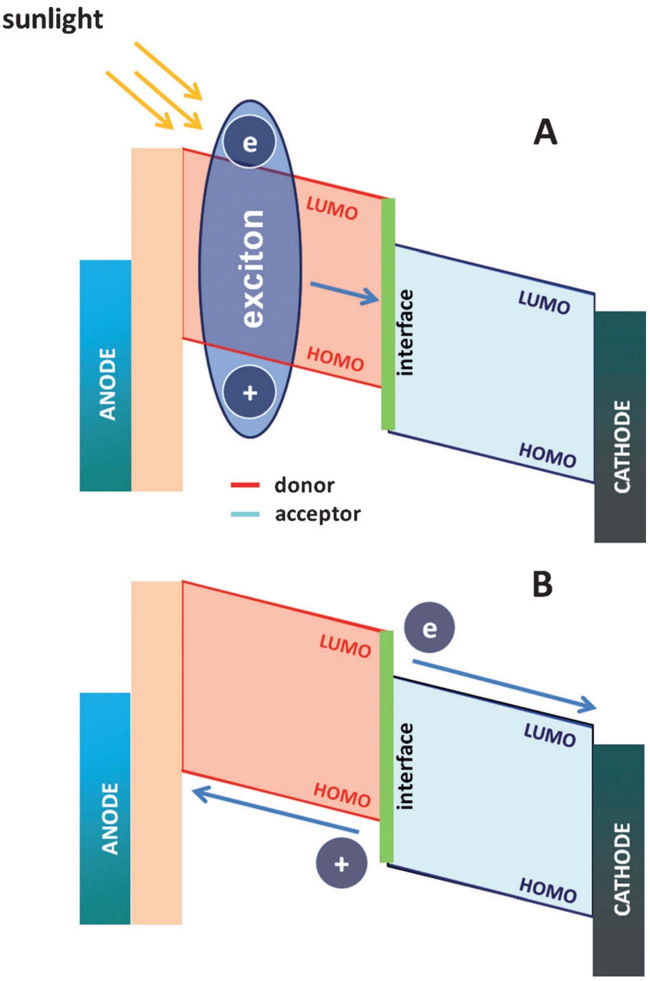

Figure 1. A) Schematic representation of steps 1. Absorption of sunlight and formation of the exciton and 2. exciton migration to the donor–acceptor interface. B) 3. Exciton dissociation into charges (electrons and holes) and 4. charge transport to and collection at the electrodes.

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cells. Therefore, the junctions of the perovskite material with the respective hole- and electron-transporting materials only facilitate charge extraction but do not contribute to charge separation. Burn, Meredith et al.[6] showed that the previously reported static dielectric constant of the $CH_3NH_3PbI_3$ perovskite was underestimated. Due to this, they could estimate an even lower exciton binding energy of roughly 2 meV, therefore confirming that these systems are predominantly non-excitonic. Additionally, these authors demonstrated that these devices show strongly suppressed recombination behavior and near-unity charge generation and extraction. Very recently, Nicholas et al.[7] showed that the exciton binding energy in the low-temperature phase of the applied $CH_3NH_3PbI_3$ perovskite is in the order of 16 meV. However, due to the frequency dependence of the dielectric constant, the exciton binding energy drops to values on the order of millielectron volts at room temperature, clearly demonstrating the formation of free charge carriers under operation conditions of the photovoltaic device.

Interestingly, in a very recent report Huang et al.[8] provided direct evidence for the non-excitonic nature of organolead trihalide perovskites. The dielectric constant was measured, and the V_{OC} variation with respect to the LUMO offset between $CH_3NH_3PbI_3$ and various fullerene derivatives was investigated. According to the literature, the exciton binding energy which allows differentiating excitonic and non-excitonic semiconductors can range from 20 to 56 meV. Even though the exciton binding energy of $CH_3NH_3PbI_3$ is larger than that of inorganic materials, it is notably smaller than those of most organic semiconductors, which are generally in the range of 0.2–1.0 eV. The authors demonstrated a giant relative dielectric constant over 500 on a low frequency of 20 Hz, thus clearly indicating that $CH_3NH_3PbI_3$ is a non-excitonic material, because the attraction forces between electron and hole pairs can be effectively broken. This finding was very recently supported by Ng, Lee et al.,[9] who showed that perovskite solar cells built with $CH_3NH_3PbI_{3-x}Cl_x$ perovskite/[60]fullerene are more similar to a n-n junction than a p-n junction, which is typical for OPVs. The authors demonstrated that the perovskite/[60]fullerene interface does not provide enough driving force for the charge dissociation process. In other words, this device is efficient due to the instant charge dissociation which efficiently produces free carriers in the perovskite film.

The above-mentioned studies unravel the photovoltaic conversion within PSCs and indicate that these new solar cells should be seen as “silicon-like” photovoltaic devices, where the absorption of incident photons results in the almost instantaneous generation of free charges (Figure 2).

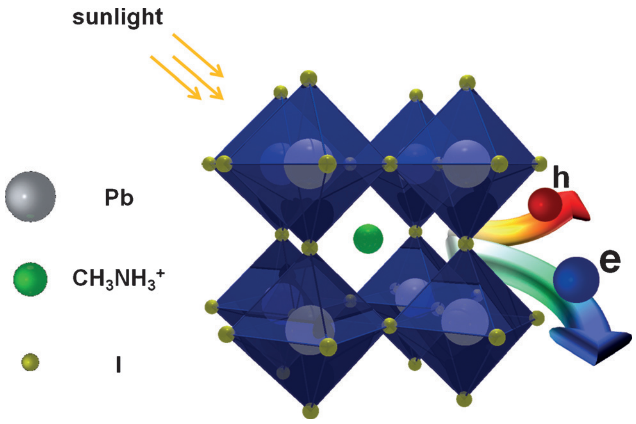

Figure 2. Schematic illustration showing the efficient free-charge generation upon photoexcitation in $CH_3NH_3PbI_3$-perovskite.

This non-excitonic nature is crucial for the development of high-performance devices. The efficient generation of free charges in one step is one of the main advantages of perovskite solar cells. In contrast, in excitonic solar cells, significant losses in energy occur through exciton migration, exciton dissociation, and charge transport and collection. While the already commercialized silicon solar cells have reached a plateau in terms of efficiency under laboratory conditions, the field of perovskite solar cells is still in its infancy and has already experienced a tremendous efficiency leap from 15 %[10] to around 20 % in two years.[11]

Thus, once this photovoltaic mechanism has been unraveled, the field is open for the investigation of a wide variety of organic compounds, such as small molecules and polymers, in order to obtain highly efficient solar cells. In this regard, a suitable energy alignment of the organic materials to satisfy the energetic requirements of the different organolead trihalide perovskites is highly recommended.

In summary, perovskite-based solar cells will play a very important role in satisfying the increasing energy demands of our society, assuring the development and quality of life for future generations.

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