A periodic hybrid DFT investigation of the perovskite/TiO_2 interface for perovskite solar cell application: from structural features to electron injection

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Abstract

Recently, many research works have focused on perovskite solar cells (PSC) since they appear as excellent potential candidates to produce clean energy, with easy fabrication and relatively high-power conversion efficiency (latest certified: 24.2%).[1] The general structure of a PSC consists of a perovskite compound as the light-absorbing material together with hole and electron transfer layers (H/ETL) and electrodes. Among the key points governing the PSC efficiency, interface properties are critical and their modeling can shed light on the working principles of these cells, potentially suggesting possible ways of improvement. In particular, at the experimental level, interface engineering has been considered and self-assembled monolayers (SAMs) obtained by facile solution-based processes are thought to induce various positive effects to PSC performances, such as on morphology modification, band alignment, trap passivation and delay of charge recombination.[2]

In this work, a periodic DFT-based computational protocol is developed and applied to model the interface properties of PSC.[3,4] We focus on the interaction between the perovskite compound methylammonium lead iodide ($CH_3NH_3PbI_3$, referred to as MAPI) and TiO_2 as an ETL, which are linked via a bidentate ligand. Based on a previous work devoted to ligand screening for PSC application,[5] 4-chlorobenzoic acid (CBA) was selected as a suitable candidate, due to its firm adsorption to the TiO_2 surface through its carboxylic group, its favorable dipole moment for suitable band alignment and its free Cl site available for perovskite binding. A periodic model of the MAPI-(110)/CBA/TiO_2 anatase (101) interface was then built and its structural and electronic properties have been computed using a periodic hybrid DFT approach. A stable interface was obtained thanks to the CBA ligand, with a favorable band alignment taking place between MAPI-(110) and TiO_2 anatase (101), resulting in an efficient electron injection from the perovskite to the semiconductor after light absorption. Overall, we show how the proposed DFT-based computational protocol can help in selecting a suitable ligand candidate for PSC application, leading to a better stability of such systems, together with improved band alignment and electron injection.

References

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