

Band engineering of nickel oxide interfaces and connection between absolute valence energy alignment and surface dipoles in halide perovskite heterostructures

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The spectacular rise of the photovoltaic power conversion efficiency of hybrid organic-inorganic perovskites to over 25% has conferred them a promising position in the field of photovoltaics and optoelectronics¹. To further improve their device performance, there is a considerable ongoing research effort on tuning their interfacial energetics with charge selective contacts along with passivating and/or functionalizing their surfaces and interfaces². Among possible charge selective contact materials, nickel oxide (NiO) is commonly used as a hole transporting layer in thin-film optoelectronic technologies based on organic or hybrid materials. Here³, we computationally scrutinize the interfacial properties of the prototype MAPbI₃/NiO heterostructure, which has shown excellent photovoltaic performance and in particular a large open-circuit voltage⁴. We study the valence band energy level alignment between MAPbI₃ and NiO considering i) the defect-free system ii) the role of defects and iii) doping. To further highlight the influence of surface dipoles on work functions and absolute valence energy alignment, we present a theoretical methodology, bridging classical electromagnetism and modern atomistic approaches, to show their intimate connection^{5,6}. We demonstrate the potentials of the methodology, through a variety of cases such as surface termination and passivation and/or functionalization. Our approaches to inspect the properties of heterojunctions, interfaces and surface dipoles transcend the limits of halide perovskites and provide computational strategies to fine-tune energy level alignments for optimizing the performance of broader families of optoelectronic devices.

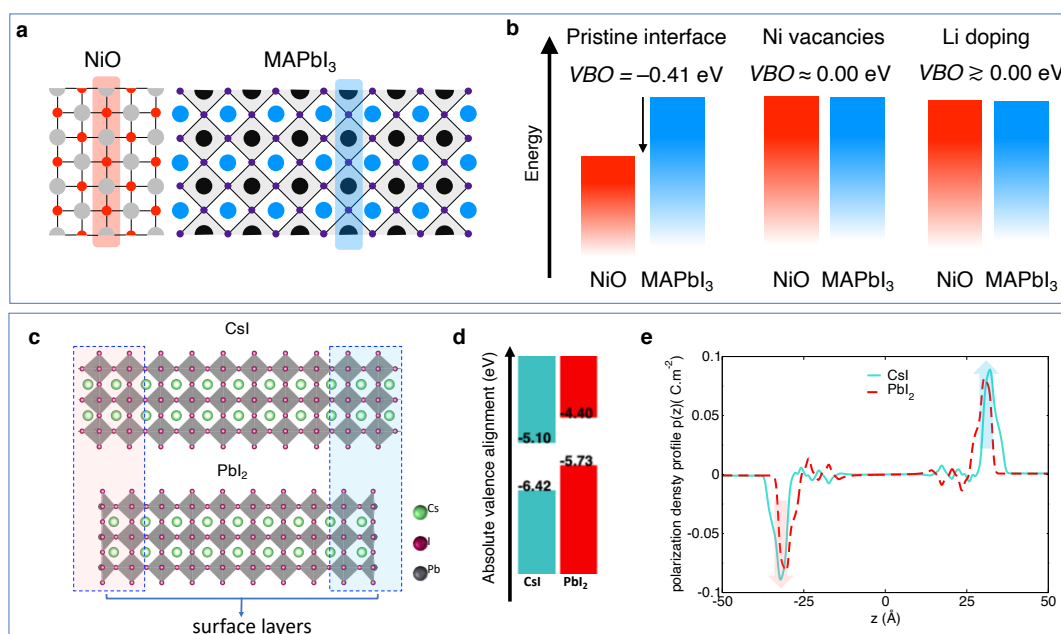


Figure 1 (a) Schematics of MAPbI₃/NiO/ interface model. (b) The valence band offset (VBO) between MAPbI₃ and NiO for the pristine interface, the interface with Ni vacancies and the interface with Li doping. Effect of surface termination on absolute energy alignments and microscopic interpretation on (c) CsPbI₃ structures with CsI and PbI₂ terminations with relaxed surface layers. The surface layers are shown by dashed rectangles on either side of the slab. (d) Computed absolute valence energy levels for CsI and PbI₂ terminated surfaces, respectively, for relaxed surface layers. (e) Polarization density profiles of the two slab systems showing different surface dipoles for relaxed surface layers. The arrows pointing the directions of the dipoles are guides to the eyes.

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References:

1. <https://www.nrel.gov/pv/cell-efficiency.html>, Accessed: 31-08-2021.
2. Schulz et al., "Halide Perovskites: Is It All about the Interfaces?", *Chem. Rev.* 119, 3349-3417, 2019
3. Traore et al., "Importance of Vacancies and Doping in Hole Transporting Nickel Oxide Interface with Halide Perovskites", *ACS Appl. Mater. Interfaces* 12, 6633-6640, 2020
4. Nie et al., "Critical Role of Interface and Crystallinity on the Performance and Photostability of Perovskite Solar Cell on Nickel Oxide", *Adv. Mater.*, 30, 1703879, 2018
5. Leung et al., "Relationship Between Surface Dipole, Work Function and Charge Transfer: Some Exceptions to An Established Rule", *Phys. Rev. B* 68, 195408, 2003
6. Traore et al., manuscript under review