Metal halide perovskite interface study for optoelectronic device application

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Introduction

Metal halide perovskites (MHPs) have emerged as promising materials for optoelectronic devices due to their exceptional charge transport and tunable band structure. However, inconsistencies in reported electrical properties and a limited understanding of these properties hinder their full potential. One key challenge is determining whether MHPs exhibit intrinsic semiconductor behavior and explaining the inconsistencies in electrical properties, ranging from n-type to p-type, observed in nominally identical materials. Additionally, the energy level alignment at 2D/3D perovskite heterostructures remains controversial, despite its critical role in device performance and stability.

This study investigates two key aspects: (1) the intrinsic electrical properties of MHPs on different substrates and the role of oxygen-induced p-type doping, and (2) the electronic structure of 2D/3D perovskite interfaces, particularly whether they exhibit type-I or type-II level alignment. These insights are essential for optimizing future perovskite-based optoelectronic devices.

Method

To explore the intrinsic electrical properties of MHPs, we fabricated perovskite films in an N_2-filled glove box and characterized their electronic structure using ultraviolet photoelectron spectroscopy (UPS). Oxygen exposure was controlled using a leak valve in the preparation chamber. All measurements were conducted after direct transfer to the analysis chamber without breaking the vacuum to exclude the extrinsic contamination. For the 2D/3D heterostructure study, we deposited PEA_2PbI_4 onto $MAPbI_3$ films and examined their energy level alignment using UPS and inverse photoelectron spectroscopy (IPES) measurements. Steady-state photoluminescence (PL) measurements as a function of excitation energy were used to investigate charge transfer dynamics across the interface.

Results

1. Intrinsic electrical properties of metal halide perovskites

To determine the semiconductor nature of MHPs, we measured the work function (Φ) and valence band maximum (EVBM) of $MAPbI_3$ films prepared under N_2 and air environments. N_2-prepared $MAPbI_3$ exhibited a substrate-dependent Fermi level shift of up to 0.9 eV, whereas air-prepared $MAPbI_3$ consistently showed a Φ of 5.11 eV and EVBM of 0.55 eV. Furthermore, oxygen was found to diffuse into the bulk of the MAPbI3 film over the rather long timescale, leading to p-doping in the MAPbI3 bulk.[1] Both intrinsic properties and p-doping effects were consistently observed in modern MHPs, e.g. $FAMAPbI_3$ and $CsFAMAPbI_3$, providing an explanation for the discrepancies in previously reported electrical properties.[2]

2. Energy level alignment of 2D Ruddlesden Popper/3D metal halide perovskite

The interface between 2D and 3D perovskites plays a crucial role in charge transport and stability. While it is commonly assumed that the $PEA_2PbI_4/MAPbI_3$ interface exhibits type-II level alignment, our UPS measurements show a type-I junction, independent of substrate work function (Φ_{sub}). This energy level alignment facilitates energy transfer from the 2D to the 3D MHPs layer, as confirmed by enhanced PL intensity of the 3D $MAPbI_3$ as a function of the excitation energy. These findings provide direct experimental evidence of type-I alignment, which is essential for optimizing interface engineering in perovskite devices.

Conclusion

This study provides critical insights into the fundamental electronic properties of MHPs and their heterostructure interfaces. We demonstrate that oxygen diffusion induces p-type doping in various MHPs, providing a pathway to explain inconsistencies in previous electrical measurements. Additionally, we reveal that the 2D/3D perovskite interface exhibits type-I energy level alignment, facilitating efficient energy transfer. These findings provide a crucial foundation for optimizing future perovskite-based optoelectronic devices while offering a fundamental understanding of electronic properties of MHPs.

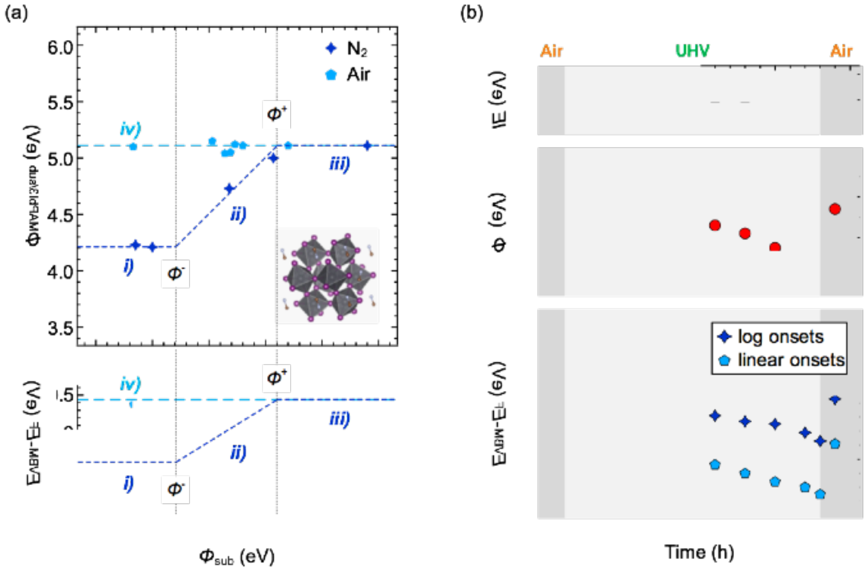

Figure 1 a) Φ values and E_{VBM} of $MAPbI_3$ films prepared in N_2 and air, as a function of Φ_{sub}, (b) electronic parameters changes of $MAPbI_3$ films upon successive air and UHV exposure for different periods.[1]

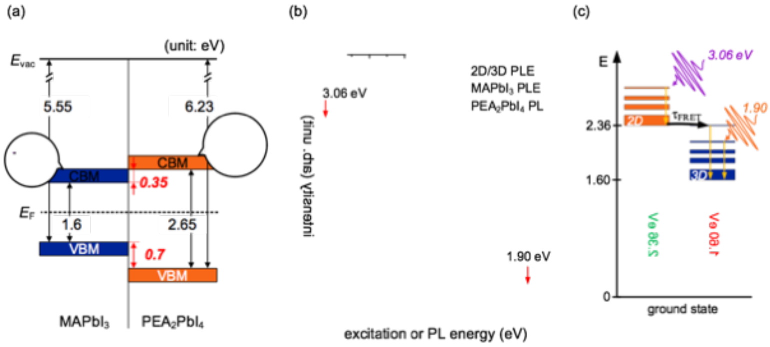

Figure 2 a) energy level diagram of the $PEA_2PbI_4/MAPbI_3$ heterostructure. b) photo-luminescence excitation (PLE) spectra of $MAPbI_3$ and 2D/3D films monitored at 1.60 eV (i.e., optical gap of MAPbI3) and PL spectra of PEA2PbI4 on quartz substrates c) schematic level diagram showing PL and energy transfer processes at the 2D/3D perovskites interface.[3]

Reference

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