Symmetry Breaking at MAPbI₃ Perovskite Grain Boundaries Suppresses Charge Recombination: Time-Domain ab Initio Analysis

Yutong Wang,† Wei-Hai Fang,‡ Run Long,*†‡ and Oleg V. Prezhdo†‡

†College of Chemistry, Key Laboratory of Theoretical & Computational Photochemistry of Ministry of Education, Beijing Normal University, Beijing 100875, P. R. China
‡Department of Chemistry, University of Southern California, Los Angeles, California 90089, United States

Supporting Information

ABSTRACT: The influence of grain boundaries (GBs) on charge carrier lifetimes in methylammonium lead triiodide perovskite (MAPbI₃) remains unclear. Some experiments suggest that GBs promote rapid nonradiative decay and deteriorate device performance, while other measurements indicate that charge recombination happens primarily in non-GB regions and that GBs facilitate charge separation and collection. By combining time-domain density functional theory and nonadiabatic (NA) molecular dynamics, we demonstrate that charge separation and localization happening at MAPbI₃ GBs due to symmetry breaking suppresses charge recombination. Even though GBs lower the MAPbI₃ bandgap and charge localization enhances interactions with phonons, electron–hole separation decreases the NA coupling, and the excited state lifetime remains virtually unchanged compared to the pristine perovskite. Our study rationalizes how GBs can have a positive influence on perovskite optoelectronic properties and advances fundamental understanding of charge carrier dynamics in these fascinating materials.
sufficiently adaptive to heal a major GB defect created in a relatively small 240 atom simulation cell. The relaxed GB structure exhibits only shallow defect states within 0.1 eV from band edges. These states localize electrons and holes, facilitating charge separation. The relaxed structure is tight with some atomic motions even reduced compared to the pristine system. Even though charges in the GB states couple more strongly to phonons than free charges, the electron–hole separation reduces the NA coupling, and the excited state lifetime remains the same as in the perfect MAPbI₃. Charge localization and symmetry breaking allows higher frequency phonon modes to couple to electrons and holes. The spectrum of the active modes is broad in both pristine and GB systems, causing rapid sub-10 fs loss of coherence in the electronic subsystem, favoring long-lived excitations.

The simulations are performed using the mixed quantum-classical decoherence-induced surface hopping (DISH) NAMD technique, implemented within the time-dependent Kohn–Sham density functional theory. The method treats the lighter and faster electrons quantum mechanically and the heavier and slower nuclei semiclassically. The DISH algorithm naturally incorporates quantum decoherence within the electronic subsystem arising due to interactions with the nuclear dynamics. The decoherence time is estimated as the pure-dephasing time of the optical response theory. The approach was applied successfully to investigate photovoltaic performance in a variety of systems, including perovskites containing dopants, defects, GBs, TiO₂ with GBs, etc.

The geometry optimization, adiabatic molecular dynamics (MD) and NA coupling calculations are carried out using the Vienna Ab initio Simulation Package (VASP). The Pedrew–Burke–Ernzerhof (PBE) functional in the generalized gradient approximation is used to treat the electron exchange and correlation interactions. Projector-augmented wave (PAW) pseudopotentials are utilized to describe the core region, and a 400 eV plane-wave energy cutoff is used. The Grimme DFT-D3 method is employed to describe the van der Waals interactions, in order to maintain system stability during geometry optimization and molecular dynamics simulations. The structures are optimized by employing the Monkhorst–Pack k-point mesh for the pristine system and the 6 × 2 × 1 mesh for the GB systems, with the 0.01 eV/Å force convergence threshold. After the geometry optimization, the systems are heated to 300 K with repeated velocity rescaling for 2 ps. Then, 5 ps adiabatic MD trajectories are obtained for the R-point in the microcanonical ensemble with a 1 fs atomic time step. To simulate the electron–hole recombination processes, 3000 geometries are selected from the adiabatic MD trajectories as initial configurations for NAMD performed using the PYNAD code.

Both pristine MAPbI₃ and MAPbI₃ with a GB contain 240 atoms, allowing equivalent representation of electronic structure and vibrational modes in the perfect and defective systems. The lattice constant of the 2 × 2 × 5 supercell of the cubic phase MAPbI₃ is 6.290 Å, in agreement with the previous theoretical value of 6.310 Å. The Σ₃ (310) GB structure is built using the same optimized cubic phase MAPbI₃. The average Pb–I bond length in optimized pristine MAPbI₃ is 3.156 Å, building with the experimental value of 3.16 Å. The GB undergoes a considerable reconstruction already at 0 K, with many bond lengths and angles adjusting to minimize the penalty for creating unsaturated chemical bonds. Upon heating to 300 K, the Pb–I framework of pristine MAPbI₃ distorts slightly, and MA molecules rotate, subject to a small barrier. Additional reconstruction of the GB region is seen at room temperature. New Pb–I bonds are formed, and MA molecules reorient driven by electrostatic interaction with the inorganic lattice.

In order to characterize nuclear dynamics in the two systems, we report the canonically averaged standard deviation of the positions of each atom type, $\sigma_i = \sqrt{\langle \mathbf{r}_i^2 \rangle - \langle \mathbf{r}_i \rangle^2}$. Here, $\langle \mathbf{r}_i \rangle$ denotes the location of atom $i$, and the canonical averaging, represented by the angular brackets, is performed over 5000 configurations from the 5 ps MD trajectories for each system. The Pb and I of the inorganic lattice are considered separately, since they support the electron and hole wave functions, while all atoms of the organic MA molecules are considered together, Table 1. A larger standard deviation indicates a stronger atom fluctuation, typically suggesting an enhanced NA electron–hole coupling.

![Figure 1. Optimized and room temperature structures of (a) 2 × 2 × 5 pristine MAPbI₃ and (b) Σ₃(310) grain boundary (GB). Each system contains 240 atoms. The GB region undergoes significant reconstruction at both 0 K and room temperature, minimizing the penalty associated with formation of unsaturated chemical bonds.](image)

| Table 1. Standard Deviations in the Positions of the Pb, I, and MA Atoms in Pristine MAPbI₃ and Σ₃(310) GB |
|-----------------|-----------------|-----------------|
| Pb    | I       | MA       |
| pristine | 0.425   | 0.508   | 0.778   |
| GB     | 0.393   | 0.534   | 0.756   |
phonon coupling. The data demonstrate that introduction of the GB has a small effect on atomic fluctuation, indicating that the reconstructed GB region is as stable as pristine MAPbI₃. Interesting correlations between motions of the inorganic and organic subsystems have been observed recently, rationalizing the unexpected enhancement of charge-carrier lifetimes in MAPbI₃ at increased temperature.¹⁵

Figure 2 shows the projected density of states (PDOS) for pristine MAPbI₃ and the Σ5(310) GB system in their optimized geometries. The PDOS is split into contributions from the I, Pb, and MA atoms. The HOMO is formed primarily by the I atomic orbitals, with minor contributions from the Pb atoms. The LUMO is of complementary origin, arising primarily from the Pb atomic orbitals. The LUMO and HOMO constitute the initial and final states for the electron–hole recombination across the bandgap. The organic components do not contribute to the band edge states, and therefore, they have no direct effect on the NA coupling. However, MA motions influence the inorganic Pb–I framework mechanically and interact with charge carriers electrostatically. The direct bandgap of pristine MAPbI₃ calculated at the R-point is 1.55 eV, showing good agreement with the experimental value for cubic MAPbI₃.⁶⁵ The Σ5(310) GB introduces shallow trap states close to the band edges and reduces slightly the HOMO–LUMO gap, Figure 2b. Other types of GBs can introduce deeper trap states.²⁰ To confirm the electronic structures obtained with the PBE functional, we performed additional calculations using the HSE06 hybrid functional. The HSE06 PDOS of the pristine and GB systems are presented in Figure S1 of the Supporting Information. The HSE06 bandgaps for the pristine MAPbI₃ and GB systems are 2.06 and 1.89 eV, respectively, and are notably larger than the experimental value of 1.52 eV.⁶⁵ Importantly, the defect states introduced by the GB are shallow at both PBE and HSE06 levels of description. Since the bandgap calculated at the PBE level shows much better agreement with experiment than the HSE06 bandgap, since the nonradiative relaxation times depend significantly on the bandgap, and since PBE is much more computationally efficient than HSE06 for periodic systems, we perform the NAMD calculations with the PBE functional.

The nonradiative electron–hole recombination rate is governed by the NA coupling between the initial and final states, and the NA coupling strength depends on overlap of the electron and hole wave functions. Figure 3 presents distribution of the HOMO and LUMO charge densities for the pristine and GB systems, at both 0 K and ambient temperature. Electrons and holes are localized in different regions of the GB. Thermal disorder enhances the localization.
GB region, leading to electron with experiment. GBs split the lattice, creating unsaturated much less at the GB than in pristine MAPbI$_3$. Since the charges are localized much more and the orbitals overlap as stretching and bending of MA molecules, are seen. The majority of the phonon modes that promote the nonradiative charge recombination and accept the energy lost by the electronic subsystem reside in the low frequency region of the spectrum. No contributions from high frequency modes, such as stretching and bending of MA molecules, are seen. The strong peak around 100 cm$^{-1}$ can be assigned to the Pb–I stretching, and the peak below 60 cm$^{-1}$ can be assigned to the Pb–I–Pb bending. Both Pb–I stretching and bending modes influence geometry of the inorganic lattice and create the NA coupling. Higher frequency peaks at around 150 and 200 cm$^{-1}$ can be attributed to librations of the organic MA cations. Since the charges are supported only by the inorganic lattice, the organic cations influence charge dynamics indirectly, either electrostatically or by mechanical coupling to the inorganic lattice. The peaks at 300 and 400 cm$^{-1}$ can be assigned to the MA torsional modes, proposed as a marker of the orientational disorder of the material. Electron-vibrational interactions involve both inelastic and elastic scattering. Quantified by the NA coupling, inelastic scattering gives energy losses from electron to phonons during the electronic transition from LUMO to HOMO. Elastic scattering destroys quantum coherence formed between LUMO and HOMO during the recombination process and is characterized by the pure-dephasing time of the optical response theory. Figure 5 gives the pure-dephasing functions calculated using the second-order cumulant approximation. Reported in Table 2, the pure-dephasing times, $\tau$, are obtained by Gaussian fitting, $\exp[-0.5(t/\tau)^2]$. The short, sub-10 fs coherence times contribute to the long charge carrier lifetimes in HOIPs, which can be understood as a manifestation of the quantum Zeno effect. The inset in Figure 5 present the unnormalized autocorrelation functions, Fourier transformed in Figure 4.

![Figure 4. Fourier transforms of the autocorrelation functions for the HOMO–LUMO energy gap in (a) pristine MAPbI$_3$ and (b) $\Sigma$S(310) GB. Many types of motions, including bending and stretching of the Pb–I lattice, and librations and torsions of MA, contribute to the signal. Figure 5. Pure-dephasing functions for the HOMO–LUMO transition in the pristine and GB MAPbI$_3$. The inset shows the unnormalized autocorrelation functions, Fourier transformed in Figure 4.]

<table>
<thead>
<tr>
<th>Bandgap (eV)</th>
<th>NA coupling (meV)</th>
<th>Dephasing (fs)</th>
<th>Recombination (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pristine</td>
<td>1.55</td>
<td>0.56</td>
<td>6.23</td>
</tr>
<tr>
<td>GB</td>
<td>1.34</td>
<td>0.44</td>
<td>5.19</td>
</tr>
</tbody>
</table>
LUMO energies to fluctuate independently of each other, leading to a large HOMO–LUMO energy gap fluctuation, reflected in the initial values of the un-ACF. The lightly higher initial un-ACF value for the GB system, inset in Figure 5, indicates that elastic electron–phonon scattering is slightly stronger and rationalizes why the pure-dephasing time is somewhat shorter, Table 2.

Figure 6 presents evolution of the excited state populations during the nonradiative electron–hole recombination in pristine MAPbI$_3$ and at the ΣS(310) GB. The recombination times, summarized in Table 2, are obtained using the short-time linear approximation to exponential decay, $f(t) = \exp \left( -t/\tau \right)$ ≈ 1 − (t/τ). The data agree with the experimental MAPbI$_3$ carrier lifetimes, ranging from tens of picoseconds to hundreds of nanoseconds. Introduction of the ΣS(310) GB has little effect on the recombination, because the GB region undergoes significant reconstruction, Figure 1, compensating for unsaturated chemical bonds and reducing the bandgap only slightly, Figure 2 and Table 2, and since symmetry breaking separates electron and hole, Figure 3, reducing the NA coupling. The result rationalizes the experiments showing that charge recombination happens primarily in non-GB regions of MAPbI$_3$ films and that GB facilitates charge carrier separation. Thus, while some GBs constitute a major source of charge carrier losses, it is possible to obtain polycrystalline MAPbI$_3$ films in which carrier losses are not accelerated at GBs, and in which GB helps to separate electrons and holes.

In summary, we have performed a time-domain ab initio NAMD simulation of the nonradiative electron–hole recombination in pristine MAPbI$_3$ and MAPbI$_3$ with a ΣS(310) GB. The study demonstrates that GBs can have a positive effect on performance of perovskite-based devices. On the one hand, GBs help to separate electrons and holes and dissociate photogenerated excitons. On the other hand, GBs do not necessarily accelerate charge recombination. The ability of the relatively soft perovskite structure to rearrange and heal unsaturated chemical bonds created in GB regions is the key property in this regard. Charges are separated because GBs break perfect crystalline symmetry and create trap states. However, because the trap states are shallow, due to reconstruction of the GB region, the charges can escape back to delocalized bands and continue long-distance transport.

Charge separation by shallow traps is also responsible for slow charge recombination, with a time scale similar to that in bulk MAPbI$_3$. In addition to defect healing, the soft, multi-component structure of MAPbI$_3$ provides a broad spectrum of phonon modes that induces rapid loss of quantum coherence during charge recombination, making it slow. The study suggests that a moderate annealing of polycrystalline MAPbI$_3$ can facilitate GB reconstruction and significantly improve its performance. The detailed time-domain atomistic analysis of charge carrier dynamics in MAPbI$_3$ advances our understanding of the key factors governing the unique properties of HOIPs.

**ASSOCIATED CONTENT**

Supporting Information
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**AUTHOR INFORMATION**

**Corresponding Author**

E-mail: runlong@bnu.edu.cn.

**ORCID**

Wei-Hai Fang: 0000-0002-1668-465X
Run Long: 0000-0003-3912-8899
Oleg V. Prezhdo: 0000-0002-5140-7500

**Notes**

The authors declare no competing financial interest.

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