Exciton Dissociation and Suppressed Charge Recombination at 2D Perovskite Edges: Key Roles of Unsaturated Halide Bonds and Thermal Disorder

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1. INTRODUCTION

Two-dimensional (2D) Ruddlesden–Popper perovskites form a new class of solar energy materials with high performance, low cost and good stability. Nonradiative electron–hole recombination is the main source of charge and energy losses, limiting material efficiency. Experiments show that edge states in 2D halide perovskites accelerate exciton dissociation into long-lived charge carriers, improving performance. Using a combination of nonadiabatic molecular dynamics and time-domain density functional theory, we demonstrate that unsaturated chemical bonds of iodine atoms at perovskite edges is the main driving force for hole localization. Chemically unsaturated Pb atoms confine electrons to a much lesser extent, because they more easily support different oxidation states and heal chemical defects. This difference between defects associated with metals and nonmetals is general to many nanoscale systems. Thermal atomic fluctuations play important roles in charge localization, even in the bulk region of 2D perovskite films, a phenomenon that is different from polaron formation. Charge localization at edges is robust to thermal excitation at ambient conditions. The separated charges live a long time, because the nonadiabatic coupling between the excited and ground states is small, under 1 meV, and quantum coherence is short, less than 10 fs. The calculations agree very well with the time-resolved optical measurements on both luminescence lifetime and line width. The detailed understanding of the excited state dynamics in the 2D halide perovskites generated by the simulations highlights the unique chemical properties of these materials, and provides guidelines for design of efficient and inexpensive solar energy materials.

Compared to 3D halide perovskites, the 2D materials exhibit greater exciton binding energies, making them more efficient light emitters. Having smaller effective masses of electrons and holes, 2D perovskites exhibit larger charge conductivities compared to their 3D counterparts. Similarly to 3D perovskites, organic cations create defects in the 2D halide perovskites. Fortunately, charge traps are quite shallow, allowing charges to escape into bands and enhancing large charge carrier lifetimes. Because of weaker dielectric screening, and therefore, stronger electron–hole interactions, compared to the 3D materials, dissociation of photogenerated excitons into free charge carriers can limit solar energy applications of the 2D perovskites. The mechanism of exciton dissociation in the 2D perovskites with the formula (BA)₂(MA)₃₋ₓPbxI₃₋ₓ has been investigated by Blancon et al. using photoluminescence excitation spectroscopy. They proposed that edges of the 2D halide perovskites accelerate exciton dissociation and generate long-lived charge carriers. Shi

Received: June 6, 2019
Published: September 6, 2019
et al.\textsuperscript{32} demonstrated the dynamic nature of the edge states maintained at finite temperatures. The nature of edge levels in the 2D perovskites is not well understood and is a subject of intense discussion in recent literature.\textsuperscript{33–37}

In this paper, we report time-domain \textit{ab initio} studies of the chemical mechanisms underlying the exciton dissociation and improved photovoltaic performance of 2D perovskites. We demonstrate that charges localize rapidly at perovskite edges, with holes exhibiting stronger localization than electrons due to asymmetry in the chemistries of the iodine and Pb atoms. A general principle to many nanoscale materials, metal atoms such as Pb heal defects much more efficiently than nonmetals such as iodines. In contrast to many other nanoscale systems, defects in 2D perovskites do not create deep traps states and are close in energy to the valence and conduction bands. In addition to edges, charge localization takes place in the bulk region of 2D films due to thermal atomic fluctuations. This spontaneous fluctuation mechanism is different from polaron formation, which occurs primarily by Coulomb interactions. Charge localization at 2D perovskite edges is maintained at room temperature. The separated charges are long-lived because the overlap between the electron and hole wave functions is very small, and quantum coherence between excited and ground electronic states is short. The charges couple primarily to phonons of the Pb–I lattice, with additional coupling at the edges to higher frequency mixed anharmonic motions involving both inorganic and organic components. Showing excellent agreement with the results of time-resolved optical experiments, the reported calculations generate important mechanistic insights into excited state dynamics of the layered 2D perovskites for optoelectronic applications.

2. SIMULATION METHODOLOGY

The simulations of the photoinduced dynamics of charge carriers in the 2D perovskites are carried out in the time-domain and at the \textit{ab initio} atomistic level of description, using a combination of real-time-history-dependent (TD) density functional theory (DFT) and nonadiabatic (NA) molecular dynamics (MD),\textsuperscript{38} and including a semiclassical correction for quantum decoherence.\textsuperscript{39} The lighter electrons are treated quantum mechanically, and the heavier nuclei are described (semi)classically. The NAMD methodology has been widely used to study of excited state dynamics in different systems,\textsuperscript{40–65} including perovskites containing grain boundaries,\textsuperscript{52} defects\textsuperscript{50} and dopants,\textsuperscript{51–53} interfaced with TiO\textsubscript{2},\textsuperscript{49,53} in contact with water,\textsuperscript{42} passivated by Lewis acids,\textsuperscript{56} exhibiting ordered electric phases,\textsuperscript{58} and having different layered structures.\textsuperscript{57} A detailed description of the theory can be found in refs.\textsuperscript{38,39,66–68} The details of the theoretical methods and simulation setup are presented in the Supporting Information (SI).

3. RESULTS AND DISCUSSION

The simulations focus on two structures representing an infinite layer of a 2D perovskite, denoted as Bulk, and a layer exhibiting an edge in one of the in-plane directions, denoted as Edge. The results are analyzed first by considering the geometric and electronic structure of the Bulk and Edge systems, followed by discussion of electron-vibrational interactions and electron–hole recombination dynamics.

3.1. Geometric Structure. The 2D perovskites of the general formula (BA)\textsubscript{2}(MA)\textsubscript{n−1}Pb\textsubscript{n}I\textsubscript{3n+1} can be related to the parent 3D MAPbI\textsubscript{3} material, in which some or all of the MA cations are replaced with long BA cationic chains.\textsuperscript{17} As a result of the substitution, MAPbI\textsubscript{3} is cut along the (110) plane, forming a stack of weakly interacting (MA)\textsubscript{n−1}Pb\textsubscript{n}I\textsubscript{3n+1} layers separated by the BA cations. If n = 1, no MA cations are left, and each layer is composed of only PbI\textsubscript{4} units. The family of the 2D structures resembles the 3D structure, involving inorganic [Pb\textsubscript{n}]\textsuperscript{6−} octahedrons tilted in the xy-plane and separated in the z-direction by the organic BA molecules.\textsuperscript{17} We focus on the simplest member of the family, (BA)\textsubscript{2}PbI\textsubscript{4}.

The edges may be terminated by either iodines or leads on either side. I-termination of both edges leads to more stable configurations, as supported by studies on perovskite quantum dots (QDs), which are stable only when QD surfaces are capped with halides.\textsuperscript{69} In order to investigate both types of termination, our main simulation is performed with one edge terminated with iodines and the other edge with leads. The additional simulations discussed in Section 3.2, with the data shown in the SI, consider other terminations, including both edges terminated with iodines. Different edge terminations should be possible in general, depending on the synthesis conditions, as exemplified for instance by synthesis of CdS QDs that can be created with Cd-rich and S-rich terminations.\textsuperscript{70,71}

Figure 1 shows geometries of the (BA)\textsubscript{2}PbI\textsubscript{4} Bulk and Edge systems relaxed at 0 K and at a representative point taken from the MD trajectory at 300 K. The optimized Bulk structure exhibits strong periodic order, with the average Pb–I bond length of 3.245 Å, in agreement with the experimental value of 3.265 Å.\textsuperscript{17,72} Thermal fluctuations perturb system geometry: some Pb–I bonds shorten while others extend. The canonically averaged Pb–I bond length in the Bulk system increases slightly, to 3.267 Å, relative to the 0 K value. The movement of the BA cations is much more significant than the fluctuation of the Pb and I atoms, in particular since only one side of the BA cation interacts strongly with more rigid inorganic frame.

The optimized structure and thermal fluctuations are quite different near the edge in the 2D perovskite, Figure 1. The Edge structure undergoes a small distortion near the edges at 0 K. The Pb–I bonds contract. The 0 K averaged Pb–I bond...
length is 3.200 Å. The corresponding canonically averaged value, 3.352 Å, is also smaller than that for the Bulk structure. The BA cations located at the edges undergo more significant fluctuations at room temperature than those in the middle of the structure.

3.2. Electronic Structure. Figure 2 presents the projected densities of states (PDOS) for the Bulk and Edge configurations in their optimized geometries. The PDOS are divided into BA, I, and Pb contributions. Similarly to the 3D MAPbI3 perovskite, the highest occupied molecular orbital (HOMO) in (BA)2PbI4 is created primarily by atomic orbitals of I atoms, whereas the lowest unoccupied molecular orbital (LUMO) is localized on Pb atoms. Organic BA groups have no contribution to the band-edge states, and therefore, they can influence the electron–hole recombination process only indirectly.

The HOMO–LUMO bandgap calculated for the Bulk configuration is 2.26 eV, which is in agreement with the previous DFT calculations and the experimental value of 2.40 eV. As expected, the pure DFT PBE functional slightly underestimates the bandgap. We increase the calculated bandgap during NAMD by 0.14 eV to match the experimental value. The HOMO–LUMO energy gap calculated for the Edge structure is 0.16 eV larger than that for the Bulk configuration, due to quantum confinement. One may have expected that creation of unsaturated chemical bonds at the Pb and I atoms near the edges should have created electron and hole trap states inside the bandgap. This is not the case. In order to be consistent with the Bulk calculations, we increase the Edge bandgap by the same 0.14 eV during NAMD.

Even though unsaturated chemical bonds created at the edges of the 2D perovskite do not create trap states within the fundamental bandgap of the material, they have significant influence on orbital localization, Figure 3, especially the unsaturated iodine bonds. The HOMO and LUMO of the optimized Bulk structure are perfectly delocalized along the inorganic layers. In comparison, the HOMO and LUMO of the Edge configuration are localized on unsaturated I and Pb bonds, respectively. The HOMO supported by I atoms is localized much more significantly than the LUMO created by Pb atoms. The situation draws analogy with the CdS QDs synthesized to have extra Cd or S atoms on the surface. Both I and S atoms require covalent bonding, and unsaturated chemical bonds involving these nonmetals produce localized states. In contrast, the Pb and Cd atoms can make metallic bonds and more easily support different oxidation state. As a result, defect arising from metal atoms are better healed, and the corresponding states are more delocalized, compared to nonmetals. Metal atoms can support multiple oxidation states, and therefore, they can eliminate some unsaturated chemical bonds and heal defects by changing their oxidation state. For example, upon creation of an iodine vacancy in MAPbI3, the two Pb atoms with unsaturated chemical bonds around the vacancy site can adjust their oxidation states in order to heal the defect and bring the defect energy from deep inside the bandgap close to the band edges. MAPbI3, with a missing I⁻ has no midgap states, because Pb atoms are in their natural Pb²⁺ states. When the vacancy becomes negatively charged, missing I⁰ or I⁻, one or both Pb atoms at the vacancy site attain the oxidation state of +1, such that the Pb defect states remain close to the conduction band. Such less common Pb¹⁺ oxidation states of Pb have been observed in organolead compounds. Other atoms capable of changing their oxidation state are also good at healing defects, e.g., the phosphorus atom in black phosphorus (BP). The fundamental difference between the halide perovskites and the inorganic QDs is that unsaturated chemical bonds terminating the system do not create states within the bandgap in the former, Figure 2, while they do in the latter. Similar phenomena are seen in other 2D materials. Transition metal dichalcogenides exhibit midgap traps in the presence of defects, while monolayer BP containing point defects and grain boundaries contains no deep trap states. The special features of monolayer BP...
can be attributed to lack of ionic character due to monoatomic composition, ability of the phosphorus atom to support different oxidation states, and significant mechanical flexibility of the monolayer that can accommodate defects and foreign species without disrupting periodic geometry.77

In order to provide additional insights into the role of the edge states in the electron−hole recombination in the 2D perovskites, we consider charge recombination between HOMO−1 and LUMO+1 in the Edge configuration, denoted Edge*. Please note that Edge and Edge* are the same structure. In addition to the Bulk system, Edge* provides another model of the realistic system, in which photogenerated charges have not yet localized on the edges. Figure 3c demonstrates the densities of these orbitals for the optimized geometry. While LUMO and LUMO+1, created by Pb atomic orbitals, are very similar, HOMO is much more localized than HOMO−1, with both HOMO and HOMO−1 arising from I atomic orbitals. This observation further supports the fact that chemically unsaturated I atoms, and not Pb atoms, are primarily responsible for the charge localization on the perovskite edge deduced from the experiments.6 The energy gaps from HOMO to HOMO−1 and from LUMO to LUMO +1 are small in the optimized geometry, Table S1. However, as temperature increases, geometric distortions break the quasi-degeneracy of these levels, and charge trapping at the edges becomes robust to thermal excitation.

In order to study the effects of thermal atomic fluctuations on charge localization, we have investigated orbital charge densities for several geometries form the MD trajectory. Figure 4 presents such densities for the 300 K geometry shown in Figure 1. These representative snapshots provide several interesting observations that are not seen in the optimized structure, Figure 3, emphasizing the importance of thermal effects. In contrast to 0 K, the HOMO and LUMO of the Bulk system are partially localized at room temperature. The localization occurs both within each layer in the xy-plane, and in the z-direction between the layers. This purely thermal effect is different from polaron formation that is widely discussed in the halide perovskite literature.81−84 Polaron formation trapped due to local structure deformation. The deformation is well-defined and is specific to the trapped charge. Thermal fluctuations also give rise to structure deformations, however, the deformations are random and change over time. Both polaron formation and random structure deformations induce charge localization, but by different mechanisms, i.e., Coulomb interactions vs thermal disorder. Large structures are required to reflect properly the geometric changes associated with polaron formation.84,85 Such large structures cannot be used in the quantum dynamics calculations, and even in a static calculation combining electron and hole polarons into a single simulation cell. Asbury and coauthors provide important experimental evidence that thermal dynamic disorder influences localization of charges that branch into large polarons and free carriers, and that localization of charge carriers in halide perovskites greatly extends charge lifetimes.86 They further argue that composition of halide perovskites can be used to control charge localization/delocalization, in order to tune charge transport and recombination, and to optimize perovskite optoelectronic properties. Similar thermally induced geometry distortions and charge localization are also found in the all-inorganic perovskites.86

Considering the Edge configuration, the HOMO supporting the hole is much more localized than the LUMO supporting the electron, just as in the optimized structure, Figure 3. The reason is the same: unsaturated covalent bonds of nonmetal I atoms create much more localized states than unsaturated bonds of Pb metal atoms. The extent of localization in the xy-plane is similar for both 0 and 300 K structures, with additional localization observed in the z-direction at ambient temperature. Note that the HOMO is always localized on iodines in the Edge configuration. The HOMO shifts from the right-hand-side at 0 K in Figure 3b to the left-hand-side at 300 K in Figure 4b, because of thermal fluctuations. Another example of HOMO in the same system for a different geometry at 300 K is shown in Figure S1, in which the HOMO is localized on the right-hand-side, as at 0 K. The average localization of the HOMO at 300 K, Figure S1, is predominantly on the right-hand-side as in the 0 K configuration, Figure 3b. In contrast to the optimized structure, for which HOMO−1 is significantly delocalized, Figure 3c, HOMO−1 of the 300 K structure is localized as much as the HOMO, Figure 4c. Charge localization occurs due to spontaneous symmetry breaking and generally varies from snapshot to snapshot. Although at any given moment along the trajectory, and even in the optimized geometry, the system is not perfectly symmetric, there is no preference for a charge to be in the upper or lower layer, on the average. We chose a representative snapshot of the MD trajectory to demonstrate that thermal fluctuations perturb geometry and favor charge localization at room temperature with respect to 0 K, Figures 3 and 4. The canonically average localizations are shown in Figures S1−S4 of the SI. The Edge structure is more mobile than the bulk material, allowing for a larger thermal disorder and giving rise to a more significant charge localization, Figure 4. In general,

Figure 4. Same as Figure 3, but for the representative 300 K geometry shown in Figure 1. Already in the infinite 2D film, the HOMO and LUMO are localized in both xy-plane and z-direction, due to thermal atomic fluctuations. The HOMO of the Edge configuration is localized much more than the LUMO, similarly to the 0 K case, Figure 3. The HOMO−1 is now localized as well, indicating that hole localization is robust to thermal excitation deeper into the valence band.
properties of nanoscale materials, such as perovskites, can change notably with temperature because they are formed due to combination of stronger (chemical bonding) and weaker (van der Waals) interactions and contain chemical defects, e.g., edges. Weaker interactions and defects are strongly susceptible to temperature induced changes. As a result, geometry changes lead to charge redistribution, formation of charge separated states and suppression of electron–hole recombination.87

In order to study the effect of edge passivation on charge localization in more detail, we considered other types of edges, including those with both edges passivated by I atoms. Representative and canonically averaged charge densities of HOMO, LUMO, HOMO−1, and LUMO+1 are shown in Figures S1–S4 of the SI. The conclusions obtained for the stoichiometric system studied in detail remain unchanged for the alternative edge passivations. In all cases, the hole is localized primarily on I atoms and the electron is localized primarily on Pb atoms, and hole localization is stronger than electron localization. All considered edge passivations indicate that iodine dangling bonds are very important for the edge driven charge localization, and support existence of long-lived charge separated states. Full characterization of edge stability under the experimental conditions is an important, but unfortunately, unsurmountable task for ab initio computations. All four considered edge terminations lead to the same conclusion: charge localization is strongly driven by unsaturated halide bonds. The conclusion is based on the fundamental properties of chemical bonding: covalent bonds are much harder to heal than metallic bonds, as has been demonstrated with other nanoscale systems.63,71

3.3. Electron-Vibrational Interactions. Electron-vibrational interactions generate elastic and inelastic scattering, both affecting the excited state lifetime. Inelastic electron–phonon scattering leads to energy exchange between the electronic and vibrational subsystems. Such energy exchange is particularly important during nonradiative electron–hole recombination, because significant amounts of electronic energy have to be deposited into nuclear degrees of freedom. Elastic electron–phonon scattering destroys coherence formed between initial and final states. Since formation of coherence is necessary for quantum dynamics, fast decoherence can strongly slow down electron–hole recombination.88 Elastic phonon-scattering is referred to as pure-dephasing in the optical response theory.89

The electron–phonon influence spectra, shown in Figure 5, characterize the phonon modes coupled to the electronic subsystem during electron–hole recombination. Overall, only low frequency vibrations are involved in the nonradiative relaxation, primarily with frequencies below 200 cm−1. No signals above 200 cm−1 are seen for Bulk. In comparison, a number of signals above this frequency are seen in the Edge system. The full spectrum of vibrational motions available in the hybrid organic–inorganic perovskites extends well above 3000 cm−1, to include stretching vibrations of C–H and O–H bonds. However, because the orbitals near the fundamental bandgap are localized exclusively on the inorganic sublattice, only slow motions of the heavy Pb and I atoms couple to the charge carriers. The dominant peak around 120 cm−1 can be assigned to the Raman active Pb–I stretching motion.17 The higher frequency modes seen in the Edge signal, Figure Sb, can be attributed to coupled motions of the inorganic sublattice and BA cations. The edge region is less rigid, more anharmonic, and less symmetric, allowing for stronger coupling between the inorganic and organic components, and relaxing symmetry selection rules.

The pure-dephasing functions89 characterizing elastic electron-vibrational scattering, are shown in Figure 6. The time scales obtained from Gaussian autocorrelation functions, whose initial values are the bandgap fluctuations squared. In general, the greater the initial value, the faster the dephasing.

![Figure 5](image.png)

Figure 5. Spectral densities obtained by Fourier transforms of fluctuations of the electron–hole energy gaps in (a) Bulk, (b) Edge, and (c) Edge*.

![Figure 6](image.png)

Figure 6. Pure-dephasing functions for the electron–hole recombination in Bulk, Edge, and Edge*. Edge and Edge* are the same structure. Edge represents the HOMO–LUMO transition, while Edge* is associated with (HOMO−1)–(LUMO+1) transition, excluding HOMO and LUMO. The time scales obtained by Gaussian fits are given in Table 1. The inset shows the unnormalized autocorrelation functions, whose initial values are the bandgap fluctuations squared. In general, the greater the initial value, the faster the dephasing.

<table>
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<tr>
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<th>bandgap (eV)</th>
<th>NA coupling (meV)</th>
<th>dephasing (fs)</th>
<th>recombination (ns)</th>
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<td>0.372</td>
<td>8.36</td>
<td>1.42</td>
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<tr>
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<td>2.77</td>
<td>0.330</td>
<td>6.67</td>
<td>3.68</td>
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Table 1. Canonically Averaged Bandgap, Absolute NA Coupling, Pure-Dephasing Time, and Nonradiative Electron–Hole Recombination Time for the Bulk, Edge, and Edge* Structures.
normalized ACF for the bandgap fluctuations, which can be used to rationalize the decoherence rate, since the pure-dephasing function is computed from the ACF. The faster decoherence in the Edge and Edge* systems are attributed to the larger initial value of the ACFs, representing energy gap fluctuation squared. Note that Edge and Edge* correspond to different excitations in the same structure. Edge refers to transition between HOMO and LUMO, while Edge* is associated with transition between HOMO−1 and LUMO+1. Edge* represents the system with edges, in which photogenerated charges have not yet localized on the edges. The gap fluctuation is more significant in Edge than Bulk, because the edge regions of the (BA)2PbI4 film are more mobile, Figure 1, and because the electron and hole are spatially separated, Figures 3 and 4. Decoherence if fast in all cases, because the phonon-induced fluctuations in the energy gaps are relatively large, on the order of 0.1 eV.

The inverse of the pure-dephasing time gives the homogeneous optical line width, \( \Gamma = h/\tau \). The pure-dephasing times reported in Table 1 correspond to homogeneous line widths on the order of 100 meV. The inhomogeneous broadening can be estimated from the magnitude of the HOMO−LUMO energy gap fluctuation along the MD trajectory, since the trajectory represents a canonical ensemble of different system structures. Calculating the gap fluctuation as the square root of the initial value of the un-normalized ACFs shown in the inset of Figure 6, we obtain inhomogeneous broadening also on the order of 100 meV. The sum of the homogeneous and inhomogeneous broadening values shows good agreement with the experimental photoluminescence line width, Figure 1H, thin film, \( n = 1 \) in ref 6. In particular, considering the Edge configuration with the 6.00 fs pure-dephasing time and the 0.0102 eVAF initial value, we obtain 110 meV homogeneous and 100 meV inhomogeneous line widths. Added together, the two contributions to the line broadening correspond well to the experimental value of 230 meV. For the bulk system, according to 8.36 fs pure-dephasing time and 0.00517 eVAF initial value, we obtain 79 meV homogeneous and 72 meV inhomogeneous contributions in Bulk. The sum of the homogeneous and inhomogeneous line widths for Bulk of 151 meV is higher than the experimental value of ∼80 meV for crystals, Figure 1H of ref 6. At the same time the trend is reproduced well: the line width is higher for Edge than Bulk. Most likely, the simulations overestimate the line width for Bulk due to small system representation, which tends to overestimate electron−phonon interactions.

3.4. Electron−Hole Recombination. The evolution of the excited state population during the electron−hole recombination dynamics that brings the system to the ground electronic state is shown in Figure 7. The time scales reported in Table 1 for Bulk, Edge, and Edge* systems have been obtained by fitting to the short-time linear approximation of the exponential decay, \( P(t) = \exp(-t/\tau) \approx 1 - t/\tau \). Note that Edge and Edge* are different excitations in the same structure.

The simulation data agree well with the experimental results. The charge recombination is several times slower in the presence of edges in the 2D perovskites. The effect arises due to smaller NA coupling and shorter quantum coherence time. In turn, both coupling and coherence times are smaller in the Edge system, because the electronic states supporting electrons and holes are localized away from each other at opposite edges, Figures 3 and 4. Spatial separation of the electron and hole wave functions decreases their overlap that influences the NA coupling magnitude, and destroys correlation between electron and hole energy fluctuations, causing decoherence. The hole is localized much more than the electron, due to the qualitative differences in the chemistries of the nonmetallic iodines and metallic Pb atoms. Charge separation by the 2D perovskite edges, without creation of charge trap states, facilitates dissociation of photogenerated excitons and provides a mechanism for improvement of solar cell performance.

Edge and surface states are common to all nanoscale materials, including perovskites. For instance, Wang and coauthors reported edge states in the 3D perovskite MAPbBr\(_3\), at room temperature. The proposed design principle, namely, that the properties of edge states are determined most strongly by nonmetal atoms, i.e., halides in the halide perovskites, should apply to other perovskites in different phases, as well as to other materials composed of metal/nonmetal atoms. CdS QDs provide another example of such principle, proven both experimentally and theoretically. This principle should apply to edges of other popular 2D materials, such as transition metal dichalcogenides, since they are also composed of metal/nonmetal atoms. The principle is general because it relies on the fundamental concepts of chemical bonding, covalent for nonmetals and metallic for metals. The principle does not apply to monoelemental 2D materials, such as graphene and black phosphorus, in which defects behave in a fundamentally different way.

4. CONCLUSIONS

Motivated by the recent experimental demonstration of efficient exciton dissociation through edge states in the 2D Ruddlesden−Popper halide perovskites, resulting in long-lived charge carriers, we have reported time-domain \( \text{ab initio} \) simulations of nonradiative charge recombination in the 2D perovskites with and without edges. The simulations have been performed by combining real-time TDDFT and decoherence corrected FSSH techniques. The results show that both electrons and holes rapidly localize at the edges, with holes exhibiting much stronger localization than electrons. The asymmetry is rationalized by differences in the chemistries of nonmetallic iodine atoms and metallic leads. In particular, unsaturated covalent bonds of iodines create strongly localized states that support holes near the top of the perovskite valence band. In comparison, Pb atoms are much more flexible in healing unsaturated bonds. Iodine bonds are more directional than lead bonds, because they involve strongly directional p-
atomic orbitals compared to the more spherical d-atomic orbitals of Pb atoms. This general principle regarding the behavior of defects associated with metals and nonmetals is typical of many nanoscale systems, for instance, semiconductor QDs. Halide perovskites are special among these materials, because unsaturated chemical bonds do not create trap states inside the fundamental bandgap. The defect states are located energetically close to the conduction and valence band edges, thereby avoiding long-term charge trapping. The findings are rationalized by the nonmetallic vs metallic properties of S and Pb atoms, they should hold for all phase of the 2D perovskites, just as they hold, for instance, for CdS QDs.\textsuperscript{70,71}

The simulations show that thermal atomic fluctuations lead to notable localization of electrons and hole even in the perfectly periodic 2D perovskite. Such localization is independent of and can be further enhanced by polaronic effects. This fact highlights that it is quite important to consider thermal disorder, since properties of nanoscale materials can change significantly between 0 K and ambient temperature. Charge localization at the edges of the 2D perovskites is maintained at room temperature, and even enhanced for the holes. Therefore, the experimentally observed charge localization at the perovskite edges is robust to thermal activation of charge carriers from the band-edge states.

The nonradiative recombination of the charge carriers separated at the edges of the 2D perovskites is slowed down due to changes in the electron-vibrational interactions. On the one hand, the NA coupling, responsible for inelastic electron–phonon energy transfer from electrons to phonons, is decreased, because it depends on the overlap of the initial and final wave functions, which also decreases due to charge separation. On the other hand, the pure-dephasing time, characterizing the duration of coherence within the electronic subsystem, is shortened, because fluctuations between the energy levels associated with separated charges become uncorrelated. Both smaller NA coupling and faster decoherence favor longer excited state lifetimes.

The electrons and holes in the halide perovskites couple primarily to low frequency vibrations of the heavy Pb and I atoms of the inorganic sublattice. The large mismatch between the phonon frequencies and the electronic energy gap makes the nonradiative electron–hole recombination a high order process, in which a single quantum of electronic energy is distributed over several dozens of vibrational quanta. Vibrations of the edge atoms are significantly more anharmonic than those of the bulk atoms. As a result, Pb–I modes couple to higher frequency vibrations of the organic cations, and several of these mixed, higher frequency modes participate in the nonradiative charge recombination.

The results of the time-domain ab initio simulations show good agreement with the experimental data, including both electron–hole recombination times and luminescence line widths. The study highlights the key roles of the chemical properties of the inorganic (nonmetallic and metallic) and organic components of the halide perovskites, electron-vibrational coupling and quantum coherence in the excited state dynamics, and provides theoretical guidance for design of high performance 2D Ruddlesden–Popper halide perovskites.

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