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Accelerated formation of iodine vacancies in CH$_3$NH$_3$PbI$_3$ perovskites: The impact of oxygen and charges

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Abstract
Defects in CH$_3$NH$_3$PbI$_3$ perovskites, oxygen species in the air, and local charges play a significant role in the long-term stability of perovskites. However, the interplay of these factors are complex and their role in the degradation of perovskites at the atomistic level is not well understood. By using density functional theory calculations and chemical bonding analysis, we study the effect of oxygen and local charges on the degradation of perovskites. We find that the easier formation of I vacancies upon oxygen and the accelerated degradation of CH$_3$NH$_3$PbI$_3$ by excess electrons via the formation of peroxide species. The creation of peroxide disintegrates the lattice of perovskites on the surfaces and possibly induces a cascade of degradation reactions that eventually destruct the perovskite lattices. We further demonstrate that the addition of holes are beneficial to prevent the formation of the peroxide, therefore can potentially improve the stability of the perovskites.

KEYWORDS
energy conversion and storage, renewable energy, solar

1 INTRODUCTION

The metal halide perovskites (MHPs) have obtained a great deal of interests in the past decade due to their high light-absorbing ability, long diffusion length, and high mobility of charge carriers.$^{1-6}$ All of these are beneficial for making efficient optoelectronic devices, such as solar cells, light-emitted diode, and lasers.$^7$–$^16$ The excellent properties of MHPs are of great importance to achieve a high power conversion efficiency of perovskite solar cells, which drastically increases from 3.8% to 25.7%.$^{17-21}$ However, the long term instability of MHPs under ambient condition (moisture, oxygen atmosphere, and sunlight illumination) impedes its commercial application, especially for the CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$) perovskite.$^{22-30}$ The oxygen can be a double-edged sword: on the one hand, the oxygen is mild in the dark condition compared with the severe corrosion of MHPs, in humidity and the oxygen treatment is often applied to improve the p-type doping of Spiro-MeOTAD in commonly fabricated perovskite solar cells$^{31,32}$; on the other hand, the oxygen induced instability under the light, for example, light induced halide segregation and lattice dissociation cannot be neglected.$^{33-36}$

Numerous studies have investigated the possible mechanisms for the degradation of MAPbI$_3$ in the presence of oxygen. Several state the oxygen molecule only physisors on MAPbI$_3$ and the degradation of MAPbI$_3$ toward oxygen is unfavorable without light illumination.$^{37,38}$ Several others reported that the synergy of oxygen and light promotes the corrosion of MAPbI$_3$, leading to the favorable reaction between oxygen and MAPbI$_3$.$^{34,37-40}$ The possible...
Despite the extension, DFT-D3(BJ) was used for the van der Waals (vdW) cut-off energy of the plane-wave basis was set to be 500 eV. Tetragonal structures for the size of the model structure should be considered carefully. We did several test calculations of 1 unit cell with 15 Å vacuum thickness, 1 × 1 unit cell with 25 Å vacuum thickness and 2 × 2 supercell with 15 Å vacuum thickness (shown in Figure S2). Overall, we found minor structural change after the enlargement of the structure except for the case of MAI-terminated defective surface. Depending on the initial structures (the positions of O2 for example) or computational setting (the size of the vacuum and unit cells), we observe the deprotonation of either one or two MA+ cations. As demonstrated in AIMD simulations in Figure S3, this particular reaction is a dynamical formation of superoxide ion (O2-) and peroxide (O22-) species under the oxygen atmosphere and light illumination causes the decomposition of the MAPbI3 structure via deprotonation reactions of MA+.34-43 Despite the extensive investigations, the underlining atomistic mechanisms of the degradation reactions and the interplay of the effect of oxygen species with local charges are still unclear.

In this paper, we use density functional theory (DFT) calculations to determine the structures and calculate the formation energies of iodine (I) vacancy with and without oxygen and the different charge quantities (from −2 to +2) on diverse pristine and defective MAPbI3 surfaces. The article is organized as follows: first, we present the computational details of DFT, chemical bonding analysis and structural models. Thereafter, because the adsorption of oxygen is the first step of the degradation of MAPbI3, we report the atomistic structures and the adsorption energies of oxygen molecules on MAPbI3. To understand the role of oxygen on the formation of I vacancies, we then investigate the relative formation energies of I vacancies at diverse surfaces (pristine and defective surfaces with different terminations) by comparing results obtained with/without oxygen species. We finally analyze the structural change, charge redistribution and chemical bonding to elucidate the combined effect of oxygen and charges and discuss the underlying mechanisms and implications of how these factors impact the stability of MAPbI3.

2 | COMPUTATIONAL METHOD

2.1 | DFT Calculations

The DFT calculations were performed with PAW pseudo-potential method as implemented in the Vienna Ab Initio Simulation Package (VASP).44-48 The Perdew, Burke, and Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) exchange correlation was utilized.49 DFT-D3(BJ) was used for the van der Waals (vdW) interactions correction.50 The cut-off energy of the plane-wave basis was set to be 500 eV. Tetragonal structures for MAPbI3 were used for the structural optimization of the bulk systems. Then, the optimized bulk structures were used to cleave 1 × 1 (0 0 1) surface slabs with four repeating unit cells (including 4 AX-layers, 4 MX2-layers and one AX-/MX2-terminated surface) in the z direction, including a vacuum of 15 Å. The defective sites and surfaces were created by removing a I atoms manually from the pristine surface. Top four layers and oxygen molecule were allowed to relax until the residual force on each atom is smaller than 0.02 eV/Å. We also did several additional calculations with force convergence criteria of 0.01 and 0.001 eV/Å. The energies show minor changes and the qualitative trends in the strength of adsorption remain unchanged (in Table S1). Considering the cost and efficiency of the calculation, we select 0.02 eV/Å as the force convergence criterion in our calculation. A 4 × 4 × 3 and 4 × 4 × 1 k-point mesh is used for bulk and surface calculations, respectively. All the possible adsorption sites are shown in Figure S1. The adsorption energies of oxygen on the surface of perovskites were calculated as following:

\[
E_{\text{ads}} = E_{\text{ads surface}} - [E_{\text{slab}} + E_{\text{O2}}]\]

(1)

\[E_{\text{ads}}\] is the energy of triplet oxygen.

The positive value of \(E_{\text{ads}}\) indicates oxygen adsorption on the surface of MAPbI3 is energetically unfavorable while the negative value of \(E_{\text{ads}}\) represents oxygen adsorption on the surface of perovskites is energetically favorable.

The defect formation energies (\(E_{\text{def}}\)) and relative defect formation energies (\(\Delta E_{\text{def}}\)) were calculated as following:

\[
E_{\text{def}} = E_{\text{tot}} [\text{iodine vacancy}] - (E_{\text{tot}} [\text{pristine/defective surface}] - \mu [\text{iodine atom}]) + qE_{\text{Fermi}}
\]

(2)

\[
\Delta E_{\text{def}} = E_{\text{def}} [\text{after oxygen adsorption}] - E_{\text{def}} [\text{before oxygen adsorption}],
\]

(3)

where \(E_{\text{tot}} [\text{iodine vacancy}]\) and \(E_{\text{tot}} [\text{pristine/defective surface}]\) are the total energies of pristine/defective surfaces with and without iodine vacancy, respectively. \(E_{\text{Fermi}}\) is the Fermi energy and \(\mu [\text{iodine atom}]\) represents the chemical potential of iodine atom.

The positive and negative values of \(\Delta E_{\text{def}}\) indicate the hindrance and facilitation of the formation of iodine vacancies after the oxygen adsorption, comparing with the surface without oxygen adsorption, respectively.

As the additional charges and vacancies are involved, the size of the model structure should be considered carefully. We did several test calculations of 1 × 1 unit cell with 15 Å vacuum thickness, 1 × 1 unit cell with 25 Å vacuum thickness and 2 × 2 supercell with 15 Å vacuum thickness (shown in Figure S2). Overall, we found minor structural change after the enlargement of the structure except for the case of MAI-terminated defective surface.
process, reflected on snapshots during the reaction showing the deprotonation of either one or two MA$^+$ cations. For the ab-initio molecular dynamics (AIMD) simulations, the Nosé–Hoover thermostat was employed at temperature 300 K. The total simulation time of each calculation is 6000 ps with a time step of 2 fs.
2.2 Chemical bonding analysis

We performed an in-depth examination of the chemical bonding in addition to the energy calculations to gain a comprehensive understanding of the energy fluctuations at each adsorption site of MAPbI$_3$ surface, the effect of charges on the interaction between MAPbI$_3$ and oxygen and the change of oxygen species. The atomic population analysis method, density derived electrostatic and chemical (DDEC6) were used. The bonds of main interest are those between oxygen and the perovskite surfaces. The chemical bonding strength was evaluated by considering both the ionic and covalent contributions to the bond. The ionic component of the bond was evaluated from the investigation of the DDEC6 net atomic charges (NACs), which quantifies the electron transfer between atoms. The negative net charge indicates the atom is obtaining electrons; the positive net charge indicates the opposite. The covalent component can be identified from the investigation of the DDEC6 bond orders (BOs). The higher the BO, the stronger the covalent bond. The DDEC6 BO is a functional of the electron and spin magnetization density distributions. Its formalism allows it to overcome limitations which are present in other BO formulations. Thus, DDEC6 BO approach exhibits good results when used in combination with various quantum chemistry methods (DFT- or wavefunction-based) and over a diverse set of materials and interactions families of sufficiently similar materials. This approach has been used to study the chemical bonding information of MHPs.

3 RESULTS AND DISCUSSION

3.1 O$_2$ adsorption on MAPbI$_3$ surface

We start with the investigation of oxygen adsorption on MAPbI$_3$ as the first step of the erosion of MAPbI$_3$. The negative adsorption energies ($E_{\text{ads}}$) indicate the adsorptions of oxygen on the surface of MAPbI$_3$ are energetically favorable. It was shown in Figure 1A,B that the $E_{\text{ads}}$ fluctuates from $-0.18$ to $-0.33$ eV (MAI-terminated pristine surface) and $-0.08$ to $-0.20$ eV (PbI$_2$-terminated pristine surface), suggesting the relatively weak adsorptions of oxygen onto all sites on the pristine surfaces of MAPbI$_3$. Compared with water adsorption investigated in our previous study, the less negative $E_{\text{ads}}$ of oxygen on pristine surface demonstrates that pristine surfaces of MAPbI$_3$ are more tolerant to oxygen than water. However, we note that oxygen strongly interacts with both MAI-terminated surface ($-2.81$ eV, Figure 1I) and PbI$_2$-terminated surface ($-2.47$ eV, Figure 1J) near an I vacancy, indicating the strong adsorption of oxygen on the defective surface than on the pristine surface of MAPbI$_3$.

The relative strength of the above mentioned adsorption of oxygen on several perovskite surfaces can be explained by their atomic structures. Figure 1C–H depict the optimized structures on all the possible adsorption sites after oxygen adsorption on pristine surfaces and Figure IIJ depict the configurations on defective surfaces (MAI- and PbI$_2$-terminated surface, respectively). We observe the bond lengths of O–O are $\sim 1.25$ Å (indicating the two oxygen atoms forming an O$_2$ molecule) on the pristine surfaces while are around $1.36$ Å (two oxygen atoms forming O$_2^-$ species) on the defective surfaces. On the pristine surfaces, it can be found that O$_2$ prefers to interact with hydrogen atoms of MA$^+$ (β and γ site, O–H: $\sim 2.00$ Å) and is repelled by Iodine atoms (α site, O–I: $\sim 4.00$ Å) on MAI-terminated surface; on PbI$_2$-terminated surface, it tends to interact with Pb atom (ε and ζ site, O–Pb: $\sim 2.95$ Å) due to the unpaired electron of O$_2$. Figure IIJ exhibit the defective surfaces of both terminations, O$_2^-$ form a shorter O–Pb bond (2.38–2.63 Å) compared with the O–Pb bond on pristine surfaces. This can be attributed to the enhanced affinity of O$_2^-$ species with MAPbI$_3^{11}$ after the acquisition of negative charge transferred from the I vacancy.

3.2 The influence of O$_2$ on the formation of iodine vacancies

I vacancy is considered the main cause of ion migration which induces several problems such as hysteresis and phase instability problems in perovskite solar cells (PSCs) under the operation condition. Moreover, photoexcited charge carriers can be trapped in the vacancy, inducing the recombination of electrons and holes, the loss current as well as the open circuit voltage and finally damaging the performance of PSCs. Considering the significance of the defect on not only the efficiency of PSCs but also its long-term stability, we here study the impact of oxygen on the formation of I vacancy on above mentioned surfaces, including MAI- and PbI$_2$-terminated pristine and defective surfaces.

To continue our investigations into the effect of O$_2$ on the formation of iodine vacancy defects, the most energetically favorable adsorption structures on both MAI- and PbI$_2$-terminated (β site and ε site, respectively) pristine surface of MAPbI$_3$ are selected. Figure 2A,B show the relative defect formation energy ($\Delta E_{\text{def}}$) before and after the adsorption of oxygen, ranging from $-0.86$ to $-3.66$ eV on MAI-terminated surface and from $-1.34$ to $-1.94$ eV on PbI$_2$-terminated surface. The negative
The value of $\Delta E_{\text{def}}$ indicates the more favorable formation of I vacancies on O$_2$@MAPbI$_3$ than on the pristine surface of MAPbI$_3$. In particular, on MAI-terminated surface, the formation of surface I vacancies (I$_1$ and I$_2$ with corresponding $\Delta E_{\text{def}}$ of $-3.66$ and $-3.23$ eV) are accelerated compared to the sub-surface ($\Delta E_{\text{def}}$: $-0.20$ eV); on the PbI$_2$-terminated surface, the I vacancies readily form not only on the surface (with $\Delta E_{\text{def}}$ from 1.34 to 1.94 eV), but also at the sub-surface with a reduced relative defect formation energy by 1.36 and 1.60 eV compared to the pristine surface, respectively. The wide range of large negative relative formation energies indicates that oxygen facilitates the formation of I vacancies, especially on the surface and subsurface of perovskite lattices, potentially leading to further destruction of the lattices beneath and further in the bulk.

The above observations in energies can be readily explained by the structural changes when comparing before and after the formation of I vacancies in Figure 2E (MAI-terminated surface), 2f (PbI$_2$-terminated surface), Figures S4 and S5. As discussed previously, only physi- sorption of O$_2$ occurs on the MAPbI$_3$ surface before the formation of I vacancies. However, after the creation of the I vacancy, the stronger interaction between oxygen and MAPbI$_3$ can be observed on both MAI- and PbI$_2$-terminated surfaces (shown in Figures S4 and S5). On the MAI-terminated surface, oxygen is attracted to the defective site in the Figure 1 so that it forms stronger hydrogen bond between the O atom with H from MA$^+$ (O–H distance being from 1.94 Å to around 1.37–1.67 Å) and the formation of O–Pb bond near the I vacancies on the surface. As for the PbI$_2$-terminated surface, either a shorter Pb–O bond (<2.40 Å) or two Pb–O bonds are formed upon the generation of I vacancies. Above structural changes can be attributed to the fact that oxygen molecules have transformed to superoxide by obtaining electrons from I vacancies, evidenced by the O–O length transformed from 1.25 Å (neutral O$_2$) to larger than 1.30 Å (O$_2^-$) on both MAI- and PbI$_2$-terminated surfaces. The strength of Pb–I bonds are weakened.
after the adsorption of oxygen (evidenced by the decreasing NAC of the Iodine atoms, shown in Figure 2C,D, Tables S2 and S3). Both effects could lead to the further degradation of the surfaces.

When making additional defects (the second one), we find again decreased relative defect formation energy when the oxygen species are involved on the defective surfaces. Figure 3A,B present the range of $\Delta E_{\text{def}}$, which is from $-2.26$ to $-2.55$ eV on MAI-terminated surface and from $-1.89$ to $-2.23$ eV on PbI$_2$-terminated surface. The decreased BOs of Pb--I bonds (Figure 3C,D, Tables S4 and S5) due to the oxygen adsorption indicates breaking Pb--I bonds cost less energy and accelerate the formation of Iodine vacancies. These results indicate that oxygen also facilitates the formation of I vacancies on the already defective surfaces. This also indicates a cascade of degradation (presented in Figures 3E,F, S6 and S7) reactions may occur once O$_2$ is adsorbed on defective surfaces.

### 3.3 Effect of charges on the oxygen-induced degradation of MAPbI$_3$

As demonstrated in Section 3.2, the structural stability of MAPbI$_3$ is largely caused by the charge transfer from I vacancy to oxygen. To gain a comprehensive understanding of the influence of the charges, we introduce additional electrons or holes of various quantities (one and two) into previously investigated O$_2$@MAPbI$_3$ pristine and defective systems. Here, we use the most favorable adsorption structures on MAI- and PbI$_2$-terminated surface ($\beta$ site and $\epsilon$ site, respectively) as examples and the structure of the pristine and the defective surfaces are summarized in Figure 4.

With the introduction of electrons, the interaction between the oxygen and MAPbI$_3$ is more robust on both terminations. It is evidenced by (i) the shorter O--H bond on the MAI-terminated surface, shortened from 1.94 to 1.86 Å (with one electron) and 1.80 Å (with two
electrons) in Figure 4A1–A3 and (ii) shorter O—Pb bond on the PbI₂-terminated surface, from 2.94 to 2.41 Å (with one electron) and 2.30 Å (with two electrons) in Figure 4D1–D3. The above results can be explained by the transformation of oxygen molecule to superoxide (O₂⁻) and peroxide (O₂²⁻) due to the accumulation of electrons near these oxygen species. Such transformation can also be reflected by the change of the BOs from 1.75 for O₂ to ~1.60 (1.50 for O₂⁻) and 1.27 (1.00 for O₂²⁻) in Table S6. The weakening of the O—O bond in superoxide/peroxide species and the accumulation of electron in the O atom give rise to stronger hydrogen bonds and Pb—O bond described above, which is undesired because this tends to deprotonate MA⁺ and distort the perovskite lattice.

As summarized in Figure 4B1–B3 and D1–D3, when one iodine vacancy is present near the O₂ species, the addition of electrons becomes more detrimental than on a pristine surface due to charge transfer on the defective surfaces, shown in Figure S8A1–A3 and D1–D3. This can be seen from the formation of O₂²⁻ (BOs of O—O is around 1.00 in Figure S8B2,C2). As a result, on the MAI termination, one and two of the MA⁺ cations deprotonate (because of the strong O—H bond), with the presence of one or two electrons (in Figure 4B1–B3); on the PbI₂ termination, the surface Pb—I bonds distort severely, partly due to the distortions caused by stronger Pb—O bonds (illustrated in Figure 4D1–D3).

In contrast, introducing holes in pristine and defective surfaces induces a slight electron depletion near O₂...
species, resulting in longer and weaker O–H and O–Pb bonds and intact perovskite surfaces (see Figure 4A–4D for the pristine surfaces, C3–C5 and Figure 4D3–D5 for the defective surfaces). In addition, the presence of the I vacancy has little impact on the rest of the lattice of both terminations and all perovskite lattices remain intact.

4 | CONCLUSION

In summary, using the density functional theory calculations and chemical bonding analysis, we investigate the stability of MAPbI3 towards oxygen with and without the presence of local charges in the form of access electrons and holes. Our calculations show weak interaction between oxygen molecule and the pristine MAPbI3 surfaces and strong interaction with defective surfaces due to the formation of superoxide, which gives rise to a strong Pb–O bond and an enhanced hydrogen bond with MA+. We find the formation of I vacancies at the presence of oxygen molecules becomes easier and is further accelerated by the presence of excess electrons, which transform superoxide species into peroxide species. The creation of peroxide corrodes MAPbI3 by accelerating the deprotonation of MA+ on MAI-terminated surface and the structural disintegration on PbI2-terminated surface. Interestingly, as unexpected, the introduction of holes has the opposite effect, preventing the formation of peroxide and hindering the deprotonation and structural destruction. Our results indicate fabricating MAPbI3 film with fewer defects and the introduction of positive local charges could be useful to avoid the degradation of MAPbI3 under the oxygen atmosphere.

CRediT STATEMENT

Qihua Li: Investigation, Writing - original draft, Writing - review & editing, Formal analysis. Silvia Gaastra-Nedea: Conceptualization, Writing - review & editing, Formal analysis, Supervision. David Smeeulers: Supervision. Shuxia Tao: Conceptualization, Methodology, Writing - review & editing, Supervision, Formal analysis.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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SUPPORTING INFORMATION
Additional supporting information can be found online in the Supporting Information section at the end of this article.

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