An Explanation for High Defect Tolerance in Metal Halide Perovskite Quantum Dots

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An Auger-like process assisted by quantum defects in metal halide perovskite quantum dots is proposed, where a charge carrier in the ground state of the quantum dot is trapped by quantum defects, resulting in a charge carrier defect being excited simultaneously and returning to the ground state of the quantum dot. It is found that the lifetime of the whole process varies from femtosecond to picosecond, depending on the radius of the quantum dot and the depth of the defect within the bandgap. Moreover, the lifetime is independent of the species of the defects, which is in good agreement with the recent theoretical prediction using ab initio non-adiabatic molecular dynamics simulation. This Auger-like process may provide a potential explanation of the high defect tolerance in metal halide perovskite materials.

1. Introduction

As the ideal candidates for many potential applications in optoelectronic and photovoltaic devices, metal halide perovskite quantum dots (MHPQDs) have spurred intense research efforts arising from their extraordinary properties, such as the bright photoluminescence covering the entire visible spectral range, strong optical absorption coefficient, and ease of fabrication. In particular, suffering from varieties of defects that are inevitable during the typical growth processes, these outstanding properties are still preserved. Meanwhile, this exceptional defect tolerance plays a key role in the high photoluminescence quantum yield. However, the underlying physics for this high defect tolerance (HDT) is ambiguous.

In fact, several mechanisms have been proposed attempting to give reasonable explanations for this HDT in metal halide perovskite materials in the past years. Tan et al. attributed it to the influence of the dipolar cation. They found that the dipolar cation reoriented in response to the local electrical field on account of the electrostatic interaction between the dipolar cation and the local electrical field generated by the defects, which reduced the capture cross-section of nonradiative recombination. From the electronic structure point of view, metal halide perovskite materials lack bonding–antibonding interactions between the conduction and valence bands, resulting in most defect levels being within the conduction or valence bands, and thus maintaining clean bandgaps. With the strong evidence of the large polaron by different experimental techniques in metal halide perovskites materials, the HDT also has been widely proposed to relate to the formation of the large polaron, which reduces the scattering of charge carriers from defects. Recently, Chu et al. pointed out that the HDT may stem from photogenerated carriers only coupled with low-frequency phonon modes, giving rise to the notable decrease of the nonadiabatic coupling between the donor and acceptor states, so both the pristine and defective systems have a long electron-hole recombination time. Although the HDT has been speculated on quantitatively by several mechanisms, as mentioned earlier, numerical evaluations for the trapping lifetime of charge carriers by defects are still very few.

In this study, we propose Auger-like nonradiative processes mediated by the neutral, positive, and negative defects in MHPQDs, respectively. We give the dependences of the lifetime of the Auger-like process on the depth of the defect in the bandgap and the types of defects. We also discuss the influence of the radius of the quantum dot on the lifetime. These theoretical results not only provide good explanation for defect tolerance in MHPQDs, but also give some insight for modulating the performance of MHPQD-based devices.

2. Theoretical Model

As shown in Figure 1, the whole process of the Auger-like recombination mediated by quantum defects can be described as follows: 1) a charge carrier in the ground state of the MHPQDs is trapped by quantum defects and 2) a charge carrier in the defects is excited simultaneously by absorbing the energy produced in the trapping process and falls back into the ground state of the quantum dot. According to the classical Auger process, this Auger-like process can be expressed as

$$\tau^{-1} = \frac{2\pi}{\hbar} |M_{\text{Direct}} - M_{\text{Exch}}|^2 \delta(E_D - E_0)$$

with

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Following the quantum defect model, the ground-state wave function $\Psi_0$ for a defect with arbitrary binding energy can be expressed as

$$\Psi_0(r) = N \left( \frac{r}{a^*} \right)^{n-1} \exp \left( -\frac{r}{\theta a^*} \right)$$

with

$$N = \frac{1}{\sqrt{4\pi a^* (\theta/2)^{2n+1} 2^{2n} (2n+1)}}$$

$$a^* = \frac{4\pi R^2}{e^2 m^*}$$

$$\theta = \frac{e}{\sqrt{8\pi a^* \Delta E}}$$

where $N$, $a^*$, and $\theta$ represent the normalization constant, effective Bohr radius, and quantum defect parameter, respectively. $m^*$ is the effective mass of an electron (or hole), and the types of defects are reflected by the parameter $\mu = A - B$ for the positive defect, $\mu = -B$ for the negative defect, and $\mu = 0$ for the neutral defect.

To calculate $M_{\text{Direct}}$ and $M_{\text{Exch}}$ directly, the term $1/|r_1 - r_2|$ is expressed in Fourier series.

$$\frac{1}{|r_1 - r_2|} = \frac{1}{2\pi} \int \frac{4\pi}{\rho^2} \exp[i \cdot (q - r_1 - r_2)] dq$$

where $q$ represents the electronic wave vector. Substituting Equation (4)–(6) into Equation (2) and (3) leads to

$$M_{\text{Direct}} = \frac{8N^2 e^2}{\pi^{3/2} R_0^6 \epsilon_0 \epsilon_r} \int \int d\rho d\rho' \frac{r_1}{a^*}^{2n-2} \sin(q \cdot r_1) \sin(q \cdot r_2) \exp \left( -\frac{r_2}{2 R_0} - \frac{2r_1}{R_0} \right)$$

for the direct term and

$$M_{\text{Exch}} = \frac{8N^2 e^2}{\pi^{3/2} R_0^6 \epsilon_0 \epsilon_r} \int \int d\rho d\rho' \frac{r_1}{a^*}^{2n-1} \sin(q \cdot r_1) \sin(q \cdot r_2) \exp \left( -\frac{r_2}{2 R_0} - \frac{2r_1}{R_0} \right)$$

for the exchange term, respectively.

In this study, we choose typical CH$_3$NH$_3$PbI$_3$(MAPbI$_3$) and CH$_3$NH$_3$PbBr$_3$(MAPbBr$_3$) quantum dots as examples to...
calculate the lifetime of this Auger-like process. The adopted values of parameters for the two materials are shown in Table 1.

3. Results and Discussion

Figure 2a,b shows the lifetime $\tau$ as a function of the depth of positive defect $\Delta E$ and the radius of a quantum dot $R_0$ in CH$_3$NH$_3$PbI$_3$ (a) and CH$_3$NH$_3$PbBr$_3$ (b), respectively. One can find that the whole Auger-like process, including the trapping and detrapping processes of a charge carrier, is very fast, on the femtosecond time scale. This ultrafast process results in an illusion that the density of charge carriers in the conduction band (or valence band) is unchanged, and it seems that defects have no influence on the charge carrier densities. Here, we must emphasize that the lifetime depends on the permittivity $\varepsilon_r$ of the electron–electron Coulomb interaction, which can vary in the range of 5–30, as proved by several experiments.[33–35] depending on the dielectric environment sensitively.[36,37] However, the lifetime ($\varepsilon_r^2\tau$) still keeps to a picosecond time scale even at $\varepsilon_r = 30$ in our numerical calculations. More importantly, the lifetime is almost independent of the depth of the defects in the bandgap when the radius of the quantum dot is smaller than 10 nm, as shown in Figure 2. Similar results are also obtained for the negative and neutral defects shown in the Supporting Information. This indicates that the lifetime does not change regardless of whether the different types of defects introduce a shallow or deep state, suggesting the “high” property of defect tolerance accurately again. Recently, Chu et al.[18] also showed that charge recombination does not depend on the types of defects and their locations in the bandgap based on ab initio non-adiabatic molecular dynamics simulation. They attributed this defect tolerance to the nature of the soft inorganic lattice of these metal halide perovskites with a small bulk modulus, which gives rise to the photo-generated carriers are inclined to couple with low-frequency phonons. Therefore, our theoretical results provide another explanation for the HDT and enrich the comparisons among different mechanisms. From Figure 2, one also can find that $\tau$ increases obviously as the radius of a quantum dot $R_0$ increases from 10 to 50 nm. It is highly probable that the carriers’ diffusion space is expanded with increasing radius of the quantum dot, suppressing the occurrence of these Auger-like processes.[18] Meanwhile, the influence of the depth of the defects on the lifetime will become more obvious as the radius increases. This means that the lifetime of the charge carrier can be modulated by the radius of the quantum dot, which is beneficial for adjusting the optical properties of quantum dots, such as the luminous intensity and the photoelectric conversion efficiency, and thus improves the performance of devices based on MHPQDs. We hope these theoretical results can trigger more experimental studies on this aspect.

4. Conclusion

We theoretically study the ultrafast Auger-like process mediated by three types of quantum defects in MAPbI$_3$ and MAPbBr$_3$ quantum dots. We find that: 1) the lifetime of the whole process maintained in the range of femtoseconds is barely sensitive to the species of defects when the quantum dot size is small, so the high tolerance of defects could be well explained by this Auger-like process; 2) the lifetime becomes longer with the radius of the quantum dot increasing; and 3) the influence of the trapping depth of defects on the lifetime is also enhanced obviously as the radius increases.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords
Auger-like processes, high defect tolerance, metal halide perovskites, quantum dots

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