Surface recombination velocity of methylammonium lead bromide nanowires in anodic aluminium oxide templates†

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Here we present successful surface passivation of halide perovskite nanowires with anodic aluminium oxide templates. The CH$_3$NH$_3$PbBr$_3$/alumina nanowires have charge carrier lifetimes of more than 20 ns and a remarkably low surface recombination velocity of $37.2 \pm 20$ cm s$^{-1}$. The ease of their fabrication and their excellent photophysical properties make them a promising candidate for integration in optoelectronic device structures.

Shockley–Read–Hall (SRH) surface and bulk recombination is detrimental to the performance of semiconductor-based devices, especially at low charge carrier injection levels. Thus, for high-efficiency devices, strategies mitigating the influence of those defects must be developed, with varying requirements for bulk and surface defects. Hybrid halide perovskites are not an exception to this rule, as their efficient performance is tightly bound to tackling the right approaches for identifying and confronting their defects. Their unusual defect chemistry and physics have enabled the rapid and simple fabrication of high-quality absorbers and emitters with long charge-carrier diffusion lengths and lifetimes, high absorption coefficients and high emission yields. Those photophysical properties in turn depend directly on the charge carrier generation and recombination dynamics. Thus, it is crucial to provide in-depth understanding of how fast and via which channels the charge carriers recombine within the perovskite light-absorber. This knowledge assists in developing strategies to minimize the structural imperfections, such as bulk and surface lattice defects for designing highly efficient optoelectronic devices. Interfacial defects facilitate the charge recombination processes and impact the overall performance of the device negatively.

Passivating the surfaces of traditional inorganic semiconductors such as Si was a milestone in achieving highly efficient solar cells. In halide perovskites, similar passivation methods have been investigated by incorporation of external materials as well as new approaches according to their special chemical structure, such as self-formation of PbI$_2$ on CH$_3$NH$_3$I$_3$ thin films through ambient exposure. Surfaces, interfaces or grain boundaries of halide perovskites have been passivated using chemical treatments via halogenated organic compounds, Lewis bases, fullerene, graphene and potassium. Many research groups investigated the application of ultra-thin metal oxide films, such as ZnO, SnO$_2$ and Al$_2$O$_3$ by atomic layer deposition (ALD) as passivation layers in halide perovskite solar cells. Note that this is different than the common use of ALD metal oxides as carrier-selective charge

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transfer layers in planar perovskite solar cells. In most of the surface passivation studies, the addition of an oxide layer improved the device performance and stability. However, little is known about the charge carrier dynamics at the perovskite/metal oxide interfaces and in particular the recombination rates and SRV have not been quantified at these interfaces.

Nanowires are promising geometries for applications in electronic and optoelectronic devices and also for case studies of dimension-dependent properties. Previously, semiconductor nanowires such as Ge, Si, and InP were studied to quantify the dynamics of charge carriers and/or investigate the effects of surface passivation. By controlling their surface to volume ratio, they provide a versatile platform to manage and quantify the contribution of surface and bulk precisely. In the past few years, perovskite nanowires have been realized via various solution and vapour-based methods. Among those, perovskite nanowires embedded in anodic aluminum oxide (AAO) templates have been successfully incorporated in efficient solar cells and photodetector devices, demonstrating the high potential of perovskite nanowires wrapped with alumina (perovskite/alumina) for future applications.

Here we study the recombination dynamics at the perovskite/alumina interface using perovskite nanowires embedded in anodic aluminum oxide (AAO) templates. The nanowires are fabricated by applying a pressure gradient across a template coated with a viscous halide perovskite precursor solution, similar to the extrusion technique we introduced previously. Fabrication from the perovskite solution directly into the AAO template avoids the exposure of the water-sensitive perovskite surface to the water precursor in a typical Al2O3-ALD process. By using templates with various pore sizes from ~150 to ~350 nm, we systematically change the surface-to-volume ratio of the final CH3NH3PbBr3 perovskite nanowires. Assuming that the bulk quality and radiative recombination rates stay constant, the changes in total recombination rates should be directly connected to the recombination at the perovskite nanowire surfaces. Time-resolved PL (TRPL) spectroscopy is used to obtain the dynamics of photoexcited carriers in the perovskite nanowire arrays. The recombination rates are extracted by fitting the PL intensity decay to a rate equation that includes radiative and non-radiative recombination. The obtained lifetime increases slightly from 24.3 ± 2.3 ns to 28.3 ± 1.5 ns when increasing the diameter by more than a factor of two. This shows the weak dependence of the PL lifetime on the nanowire diameter, suggesting a very low surface recombination velocity (SRV). By fitting these TRPL results to a simple recombination model, we extract an SRV of 37.2 ± 20 cm s−1, indeed much lower than the value measured for unpassivated surfaces of single crystal CH3NH3PbBr3 perovskites (~105 cm s−1). These results indicate that alumina provides excellent passivation for CH3NH3PbBr3 perovskite nanowires. This structure can be extended to incorporation into future devices.

To fabricate the perovskite/alumina nanowires, we employed a differential-pressure-driven process similar to the extrusion method introduced previously. However, when the perovskite solution inside the AAO pores reaches the AAO top surface, the process is terminated (before nanowire extrusion), as schematically shown in Fig. 1a. The perovskite solution fills the nanopores of the AAO template and evaporation of the solvent leaves the perovskite/alumina nanowires inside the AAO pores. Fig. 1b shows the SEM image from the bottom surface of the template prior to filling with perovskite, whereas the SEM image in Fig. 1c indicates the filling of the pores after the application of a pressure gradient. Conductivity measurements (Fig. S1†) and cross-sectional SEM images (Fig. S2†) of the filled AAO templates show that the perovskite is extended through a large fraction of the AAO pores (see the ES†). This simple method provides highly ordered arrays of perovskite nanowires with tuneable lengths (determined by the AAO thickness) embedded in a transparent medium with high surface passivation potential.

The optical properties of the perovskite/alumina nanowires are characterized with steady-state PL (405 nm excitation) and absorption measurements (Fig. 2a). The emission peak at 540 nm (2.29 eV) matches the band gap of CH3NH3PbBr3. The nanowire arrays with different diameters, but the same length (50 μm), have similar PL and absorption spectra. Finite-difference time-domain (FDTD) simulations are performed to study the light intensity distribution and absorption in perovskite/alumina nanowire arrays with various diameters, as presented in Fig. S4. The electric-field intensity (|E|2) upon excitation with short-wavelength light (485 nm) decays quickly within the first 5 nanometers away from the surface for all the nanowire arrays with different diameters. The simulated absorption spectrum is in agreement with the experimental absorption data shown in Fig. 2a.

We used three templates with average pore diameters of 150.4 ± 35.7, 208.2 ± 34.8 and 361.7 ± 20.4 nm and filled them with CH3NH3PbBr3 nanowires to study the charge

![Fig. 1. CH3NH3PbBr3 nanowires embedded in the AAO template. a) Schematic of the AAO template before and after filling with the perovskite solution. b) SEM images of the bottom side of the template before and c) after the pores were filled with the solution. The scale bars correspond to 2 μm.](image-url)
carrier dynamics and the contribution of the perovskite/alumina interface in the recombination mechanism. By decreasing the nanowire diameter and keeping the bulk recombination constant, we increase the relative contribution of the surface to the overall recombination process. Since all the samples were prepared from the same solution batch at the same time, and also measured at the same time, we expect the bulk quality and defect densities to be comparable for all of them. Therefore, changing nanowire diameters would affect the non-radiative recombination because of the higher density of trap states on the surface. Here we assume that there is no radiative channel in trap-assisted recombination and the only radiative process leading to emission is the bi-molecular recombination of two charge carriers. Therefore, the decay of PL as a function of time can be written as:

$$PL(t) = AK_2n(t)^2 + bcg$$

where $A$ is the collection efficiency, $n(t)$ is the charge carrier density as a function of time and $bcg$ is the background. Here, $k_2$ is the bimolecular recombination rate coefficient defined via the decay of charge carriers over time, as formulated below:

$$\frac{dn(t)}{dt} = -k_1n(t)^3 - k_2n(t)^2 - k_{bc}n(t)$$

where $k_1$ is the recombination rate coefficient associated with the monomolecular trap-assisted recombination and $k_2$ is the Auger recombination rate coefficient.

We measured the PL($t$) of the nanowire arrays with time-correlated single photon counting (TCSPC) over more than 8 different spots on each sample (details in the ESI†). A blue laser (485 nm) with a fluence of 8.3 $\mu$J cm$^{-2}$ excited the samples and generated an initial charge carrier density of $3.2 \times 10^{17}$ cm$^{-3}$. The calculation of carrier density is explained in detail in the ESI. At this carrier density, the role of Auger recombination is considered negligible. The representative PL decay curves of each sample are shown in Fig. 2b. We solved eqn (2) for $n(t)$, disregarding the Auger term, and inserted the result in eqn (1):

$$\tau = \frac{1}{k_1 + k_{bc}}$$

The lifetime is relatively stable, increasing only slightly with diameter. Thus the relative surface contribution to the overall charge carrier recombination is small for the high surface passivation levels obtained here.

### Table 1

<table>
<thead>
<tr>
<th>$d$ (nm)</th>
<th>$k_1$ ($\times 10^6$ s$^{-1}$)</th>
<th>$k_2$ ($\times 10^{-10}$ cm$^3$ s$^{-1}$)</th>
<th>$\tau$ (ns)</th>
</tr>
</thead>
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<tr>
<td>150.4 ± 35.7</td>
<td>3.71 ± 0.58</td>
<td>1.32 ± 0.24</td>
<td>24.3 ± 2.3</td>
</tr>
<tr>
<td>208.2 ± 34.8</td>
<td>3.99 ± 0.92</td>
<td>1.31 ± 0.19</td>
<td>26.9 ± 3.5</td>
</tr>
<tr>
<td>362.7 ± 20.4</td>
<td>2.10 ± 0.29</td>
<td>1.06 ± 0.06</td>
<td>28.3 ± 1.5</td>
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</table>
In the long nanowires studied here, the diameter is essentially the identifier of the surface area to bulk volume. In order to discover the exact dependence of the recombination on the surface, we developed a model to relate the carrier lifetime to the nanowire diameter.

In the following, we assume a charge carrier diffusion length in CH$_3$NH$_3$PbBr$_3$ that is larger than the radius of the nanowires$^{35}$ and hence a homogenous carrier concentration inside each individual nanowire and among all nanowires inside the laser spot. In this model, the surface recombination velocity is essentially a rate parameter that, together with bulk recombination, reduces the photo-generated carrier concentration observed via PL. Specific carrier gradients inside the nanowire, leading to complex carrier flow patterns are neglected. For a certain geometry, the total recombination is composed of two terms – bulk and surface – as shown below:

$$ R_T = VR_B + AR_S $$

(5)

where $R_T$ is the total recombination rate, $V$ is the volume, $A$ is the surface area, and $R_B$ and $R_S$ are the total recombination rates in the bulk per unit volume and at the surface per unit area. Considering the geometry of the nanowire as a cylinder with radius $r$ and length $l$, the equation above can be written as:

$$ R_T = \pi r^2 l (B + S_{air}/l) + 2\pi r (S_{alumina}) $$

(6)

where $B$ is the bulk recombination velocity, $S_{alumina}$ and $S_{air}$ are the rate at which the charge carrier move towards the nanowire interfaces (SRV) with alumina and air, respectively. Since $B$ and $S_{air}$ have the same dependence on the radius, we group them together as an effective bulk recombination term ($R_B$). By dividing both sides of eqn (5) by $\pi r^2 l$ (the nanowire volume), we end up with eqn (7), which allows us to extract $S_{alumina}$ from the slope of the recombination rate versus the inverse of the nanowire radius:

$$ R = R_B + \frac{2S}{r} $$

(7)

where $R$ is the recombination rate per unit volume given by $R(n, l) = k_2 n + k_1$ and by definition, is the inverse of the charge carrier lifetime ($1/\tau$). Therefore, eqn (7) is rearranged in the final form:

$$ \frac{1}{\tau} = R_B + \frac{2S}{r} $$

(8)

The inverse of the carrier lifetime is proportional to the inverse of the nanowire radius, where the slope of the line is $2S$, and the $y$-intercept is the effective bulk recombination rate. This model shows that the lower the slope is, the less the nanowire wall surface contributes to the recombination rate. Therefore, if a perfect passivation of the surface is provided, the line would be horizontal with slope zero, and recombination stemming only from the bulk and top surface. A similar approach using the continuity equation was implemented before by Léonard et al.$^{31}$ and Dan et al.$^{33}$ and the same linear relation of the recombination rate and nanowire diameter was derived, as also explained in the ESI.$^*$

Fitting eqn (8) to the inverse of the average lifetimes (calculated from eqn (4) for more than 8 experiments for each sample) versus the inverse of the nanowire radius results in an SRV of $3.7 ± 20$ cm s$^{-1}$ and a bulk recombination rate of $3 \times 10^7 $ s$^{-1}$ at the initial carrier density of $3.2 \times 10^{17}$ cm$^{-3}$ (Fig. 3a). The error is the standard deviation of SRV extracted from 10$^6$ linear fits of the averages of 5 randomly selected data points at each nanowire radius. This result shows that at this carrier density, the recombination is dominated by the bulk (with possible contributions from the top surface), and the side wall surface is well passivated. This value is considerably lower than SRVs reported in various studies for unpassivated CH$_3$NH$_3$PbBr$_3$ single crystals$^{13,44,48,49}$ (1.6–6.7 × 10$^3$ cm$^{-1}$) and lower but in the same range as reported for the passivated surface of CH$_3$NH$_3$PbBr$_3$ single crystals with UV-O$_3$ treatment (64 cm s$^{-1}$).$^{48}$ Fang et al.$^{50}$ reported an unusually low SRV of 4 cm s$^{-1}$ for the CH$_3$NH$_3$PbBr$_3$ single crystals by controlling the physisorption of oxygen and water molecules on their surface.

We should note that SRV is a facet-dependent parameter. While single crystals of CH$_3$NH$_3$PbBr$_3$ have (100) facets because of their cubic structure, the nanowire walls have higher index facets. Fig. S3$^*$ shows the X-ray diffraction (XRD) pattern of the CH$_3$NH$_3$PbBr$_3$/AAO nanowires. The (100) diffraction peaks are more pronounced which indicates that the nanowires within the AAO pores are grown in the <100> direction. This indicates that the nanowire side walls have higher index facets. Most semiconductor nanowires, such as Si$^{33}$ and Ge,$^{31}$ have SRVs 2–3 orders of magnitude higher than what is reported in this study. Obtaining the incredibly small SRV value of $3.7 ± 20$ cm s$^{-1}$ for high index facets of perovskite nanowires confirms the good passivation that

![Image](https://example.com/image.png)

**Fig. 3** Modeling the surface recombination velocity (SRV) of perovskite/alumina using nanowires with various diameters. a) Recombination rate (1/τ) versus inverse of nanowire radii. The lifetime is calculated from eqn (4) for the initial carrier density as performed in the TRPL experiment. The dashed line shows the linear fit of eqn (8) to the experimental data. The equation achieved from the fit is written above the line. The slope is equal to $2^*SRV$ and the $y$-intercept is the effective bulk recombination. b) The estimation of SRV and total bulk recombination for various carrier densities from $10^{15}$ to $10^{18}$ cm$^{-3}$. With increasing carrier density, SRV increases, but the effective bulk recombination stays dominant.
alumina provides. We reported previously a slight deviation of the lattice constant from the theoretical value for a perfect cubic crystal structure in extruded CH$_3$NH$_3$PbBr$_3$ nanowires. This might be due to the constrained growth environment of the perovskite nanowires within the AAO pores which may exist in CH$_3$NH$_3$PbBr$_3$/AAO nanowires as well. Further research is required to address the effects of constrained microstructures on the photo-physical properties of perovskite nanostructures.

The SRV depends not only on surface trap states (their type and density), but also on the charge carrier density.$^5$ Therefore, we expect an increase in SRV with increasing carrier density. We used the same recombination coefficients in Table 1, and plotted various total recombination lifetimes versus the nanowire radii in Fig. 3b for charge carrier densities of $10^{15}$–$10^{18}$ cm$^{-3}$. A higher carrier concentration is not selected because of the increasing contribution of Auger recombination with higher intensities,$^5$ which is not included in our model. By fitting eqn (8) with the different carrier densities to the dependence of the lifetime on the nanowire radius, as shown in Fig. 3b, we obtained the respective surface and effective bulk as summarized in Table 2. The last column of this table shows that increasing the surface density effectively makes the contribution of surface recombination to the total recombination rate ($S/d + R_c$) smaller.

### Conclusions

In this study we fabricated long CH$_3$NH$_3$PbBr$_3$ nanowire arrays embedded in AAO templates (perovskite/alumina nanowires) using a simple solution technique by suction of the perovskite solution through the AAO pores. The charge carrier recombination mechanism of the perovskite/alumina nanowire arrays was studied with time-resolved PL spectroscopy. Fitting of the PL intensity decay to a rate equation that includes radiative (bimolecular) and non-radiative (monomolecular) recombination was used to obtain the recombination rate coefficients. We estimated a charge carrier lifetime of more than 20 ns at the initial carrier density of $3.2 \times 10^{17}$ cm$^{-3}$ for nanowires with various diameters. The inverse lifetimes increase linearly with decreasing nanowire diameter. This data was fitted to a model to extract a very low SRV of $37.2 \pm 20$ cm s$^{-1}$ at the CH$_3$NH$_3$PbBr$_3$/alumina interface. The low SRV of passivated nanowires in comparison with that of unpassivated CH$_3$NH$_3$PbBr$_3$ single crystals ($\sim 10^3$ cm s$^{-1}$)$^{44,49,52}$ ensures that despite the large surface of perovskite nanowires, their surface was not dominant in recombination processes.

The presented results here confirm the passivation effect alumina provides for hybrid halide perovskites and quantify the surface recombination velocity at the perovskite/alumina interface for the first time. This study presents a simple systematic method for the passivation of perovskite surfaces, without the need for ALD deposition of Al$_2$O$_3$. Further studies to compare the perovskite nanowires passivated with ALD and the ones embedded in AAO templates will provide a comprehensive picture of the similarities and differences of these two methods.

### Conflicts of interest

There are no conflicts to declare.

### Acknowledgements

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### Notes and references

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### Table 2: Surface (S) and effective bulk (R$_c$) recombination velocities for CH$_3$NH$_3$PbBr$_3$/alumina nanowires at different carrier densities. S and R$_c$ are fit parameters, as shown in Fig. 3b. $S/(R_c d + S)$ is the contribution of surface recombination to the total recombination for a representative nanowire with an average diameter of $d_{av} = 200$ nm

<table>
<thead>
<tr>
<th>$n$ (cm$^{-3}$)</th>
<th>$S$ (cm s$^{-1}$)</th>
<th>$R_c$ (s$^{-1}$)</th>
<th>$S/(R_c d_{av} + S)$ (%)</th>
</tr>
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<tr>
<td>$10^{15}$</td>
<td>10.7</td>
<td>$10^6$</td>
<td>34.4</td>
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<tr>
<td>$10^{16}$</td>
<td>12.3</td>
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<td>$10^{17}$</td>
<td>27.7</td>
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</tr>
<tr>
<td>$10^{18}$</td>
<td>182.2</td>
<td>$9 \times 10^7$</td>
<td>9.2</td>
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