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Electronic Supplementary information

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

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Experimental methods

Preparation of perovskite solution: The CH_3NH_3Br was synthesized and recrystallized using a previously reported protocol.[1] 3M $CH_3NH_3PbBr_3$ solution in dimethyl sulfoxide, DMSO (Sigma-Aldrich, anhydrous, purity ≥ 99.5%) was prepared by mixing CH_3NH_3Br with $PbBr_2$ (Sigma-Aldrich, purity ≥ 98%) in 1:1 molar ratio. The solution was aged at least for 2 weeks, and heated up to 70 °C and stirred with a magnetic stirrer prior to use.

Nanowire preparation: The solution was drop-casted onto AAO templates with various pore diameters and 50 μm thickness. The pores are accessible from both sides. The solution is pulled through the template *via* an extrusion method, while the template was placed on a PDMS block with a hole connected to a low-pressure line and sealed with an O-ring. A pressure gradient (~50-100 mbar versus atm pressure) was created via a syringe connected to the hole. To ensure the nanowires stayed within the pores, the extrusion was timed using SEM characterization. Then the templates were carefully transferred to a hot plot and annealed at 125°C to evaporate the solvent and form the perovskite nanowires within the AAO pores.

Scanning electron microscopy (SEM): SEM images were taken with a FEI Verios 460 at 5 kV accelerating voltage, with a through-the-lens detector (TLD) for the top view image in Figure 1b) and the mirror high energy detector (MD) for the side view image (Figure S2).

Steady-state photoluminescence: We measured the PL spectra of perovskite nanowires in the AAO template using a WITec Alpha300 SR confocal imaging microscope. The sample was excited with a 405 nm diode laser (Thorlabs S1FC405) through a NA 0.9 objective and the luminescence was collected in reflection using a spectrometer. The calibration of the spectral response of the collection optics, fiber, and spectrometer was done with a standard mercury light source, and the spectrum was corrected accordingly.

Absorption measurement: We used a home-built integrating sphere setup consisting of a supercontinuum Fianium WL-SC390-3 laser, sent through an acousto-optic tunable filter (Fianium AOTF-V1-N1) to measure the absorption of the perovskite/AAO nanowires samples. The beam was focused through the objective (Mitutoyo M PLAN APO NUV 50X, NA 0.42) onto the mounted substrate. The spot radius was ~650 nm.

Time-correlated single photon counting: The time-resolved PL (TRPL) of nanowire arrays was measured with the time-correlated single photon counting (TCSPC) technique. In this method, a pulsed laser at 485 nm (PicoQuant PDL 828) is used to excite the samples and the luminescence of the sample is collected over multiple cycles of excitation and emission using a single photon counting detector (MicroPhoton Devices, MPD-5CTD) and a picosecond time analyzer (PicoQuant HydraHarp 400). The repetition rate of the laser can be tuned from 0.5 to 40 MHz using a PicoQuant LDH-D-C-485. We chose the repetition rate of 1 MHz for this experiment. The excitation density was controlled with adjusting the power of the laser and using a series of neutral density filters. The power for the experiment was 0.06 µW. A long pass filter (ET500LP, Chroma Tech) blocked the laser and allowed the emission of the samples to pass through to reach the detectors. The measurements were all done at the ambient condition.

In each sample more than 8 different 20x20 µm^2 regions were scanned over 256x256 pixel, where in each pixel the PL intensity decay was collected. The PL decay curve was integrated over the whole scanned area and fitted with the model presented in Equation 3 of main text to extract the recombination coefficients for each region. The recombination coefficients presented in Table 1 of the main text are averages over all the measured regions for each sample, and the error bars are standard errors of the mean.

Evidence of AAO pore filling with perovskite

In principle, if the nanowires are continuously expanded from the top to the bottom of the AAO templates, the vertical conductivity of the templates should increase dramatically, comparing the empty and filled templates. To check the top-to-bottom conductivity of the templates, we coated thin films of Ti on the both sides of an empty and a perovskite-filled template. The edges were masked during the coating to make sure that the only electrical pathways between the two bottom and top surfaces is the bulk template in between the Ti electrodes. Current-voltage (I-V) measurements revealed that the empty AAO is insulating as expected (the small current comes from capacitive charging) and the conductivity of the filled template is a three orders of magnitude higher than the empty one. Moreover, the filled template generated photocurrent under 1 sun AM1.5 illumination as an indication of photoconductivity of perovskite nanowires (**Figure S1**).

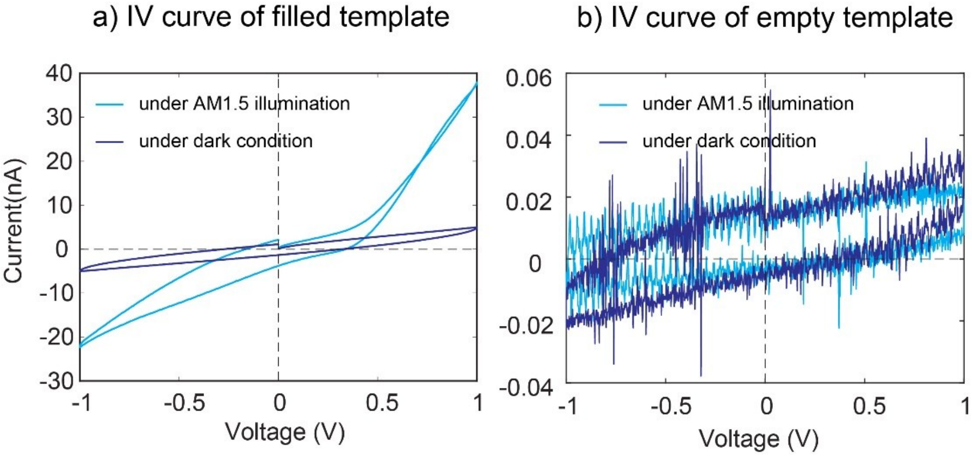

Figure S1. *a) The I-V test of a filled template with perovskite, with thin electrodes coated on the top and bottom of it. b) The I-V curves of an empty AAO template with electrodes on the bottom and top. Dark and light blue lines represent the I-V curves with and without illumination, respectively. The similar curves under both conditions in panel b indicate the insulating and non-photoconductive nature of the empty AAO template.*

Another evidence for the filling of the AAO pores with perovskite solution are cross-sectional SEM images taken with MD detectors (**Figure S2**). The MD detector highlights the compositional and topographical contrasts. The brighter lines are attributed to the perovskite containing heavy Pb elements. The apparent breaks in the cross-section image can be explained by a cleavage plane that is not perfectly aligned with the pores. This can be seen from periodic breaks as expected from a tilted cleave with continuous nanowires.

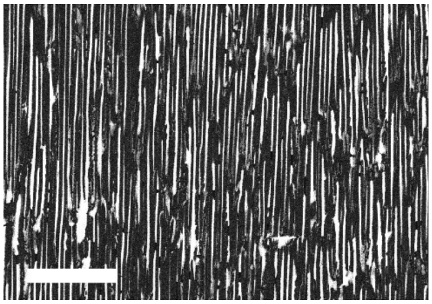

Figure S2. The cross-sectional view of the filled template taken with the MD detector of the SEM. The bright lines show perovskites solution due to the heavy Pb atoms. The scale bar is 5µm.

X-ray diffraction (XRD) pattern of $CH_3NH_3PbBr_3$/AAO nanowires

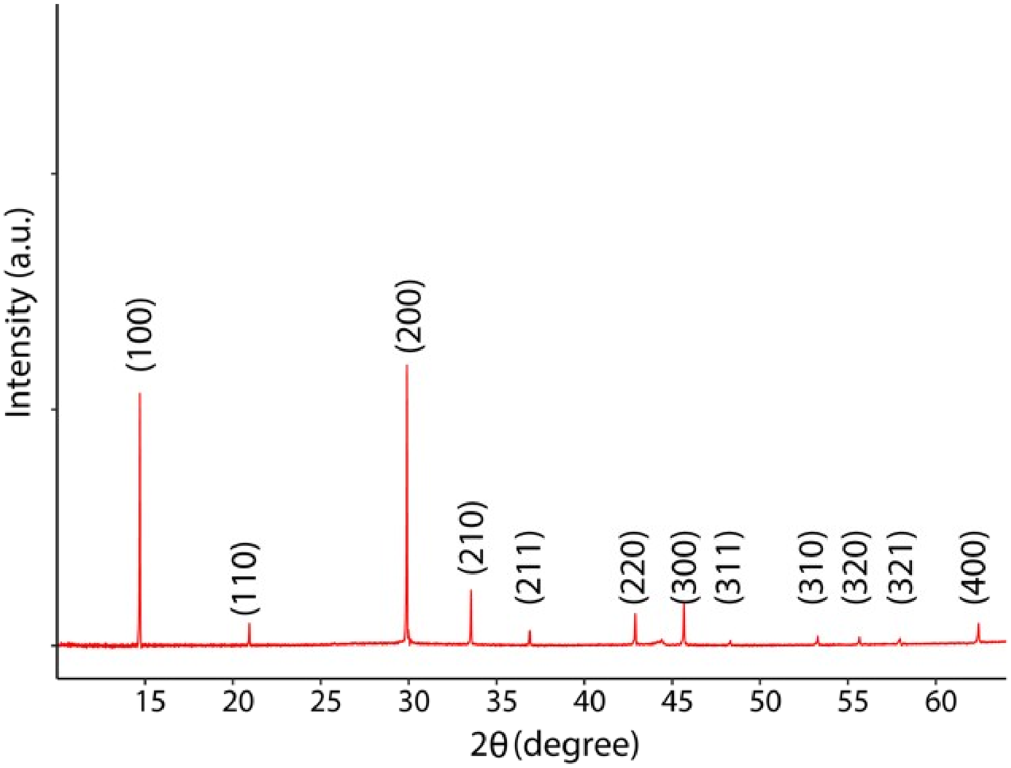

Figure S3. X-ray diffraction (XRD) pattern of perovskite nanowire array within the AAO template. The diffraction peaks of (100), (200), (300) and (400) crystal planes are more pronounced than the other planes. This indicates that most of the nanowires are aligned along the same crystallographic axis and the growth direction of the wires within AAO pore is <100>. As a result, the nanowires wall have higher index facets. Other diffraction peaks might originate from residual perovskite microcrystals formed on the AAO top surface during fabrication.

Calculation of initial charge carrier density:

We calculated the initial charge carrier density according to:

$$n_0 = \frac{N_{photons} \times A}{t}$$

Where $N_{photons}$ is the number of photons per pulse calculated from the repetition rate (1 MHz), the laser power density (8 W cm^{-2}) and photon energy at 485 nm excitation, t is the effective sample thickness and A th absorption at the excitation. A is considered 85% according to the absorption spectra measured for nanowire arrays (Figure 2a). Since the sample thickness (AAO thickness 50 µm) is much larger than expected diffusion length of the charge carriers, the effective thickness is assumed as the longest distance the charge carriers may travel. According to the reported charge carrier diffusion length of $CH_3NH_3PbBr_3$ coated with ALD alumina[2] we considered it to be 500 nm. We assumed that the initial charge carrier density is the same for all samples with different pore sizes.

Fitting procedure of TRPL data to the mathematical model

For the fitting, we normalized the initial PL (at $t=0$) and carrier density (n_0) to 1, and removed the background by subtracting the average of data points before excitation from the PL decay data. We could fit the data by only taking mono- and bimolecular recombination into account, therefore we believe Auger recombination did not play a role in the recombination dynamics.

Calculation of SRV from continuity equation

A diameter-dependent carrier lifetime has been modeled previously for nanowires[3–5] based on the solution of the continuity equation for an infinitely long cylinder with diameter d:

$$\frac{\partial n(r,t)}{\partial t} = D\nabla^2 n(r,t) - \frac{n(r,t)}{\tau_b}$$

Where $n(r,t)$ is the photoexcited excess charge carrier density, D is the diffusion constant, r is radial coordinate and τ_b is carrier lifetime in the bulk. The boundary condition for this equation is given by:

$$-D\left(\frac{\partial n(r,t)}{\partial r}\right)_{r=d/2} = S \cdot n(d/2,t)$$

Where electron and holes recombine with the velocity S at the surface. Solving the above equation results in an exponential time decay of the carrier density given by:

$$\frac{1}{\tau} = \frac{1}{\tau_b} + \lambda$$

where λ comes from:

$$D\,\lambda J_1(\lambda d/2) = S J_0(\lambda d/2)$$

J_0 and J_1 are 0th and 1st order Bessel functions. If we assume $S \ll D/d$, it is valid to use the small argument behavior of the Bessel function:

$$J_n(a) \approx \frac{1}{2^n\, n!} a^n$$

So λ=4S/d . Therefore, we have:

$$\frac{1}{\tau}=\frac{1}{\tau_b}+\frac{4S}{d}$$

Which is essentially the same as Equation 7, with the difference of the effective bulk recombination introduced in the main text..

In order to check the validation of the assumption S $\ll$ D/d, we obtained D from $L_{diff}=\sqrt{D\tau_{eff}}$, where L_{diff} is diffusion length and τ_{eff} is carrier effective lifetime. The L_{diff} was extracted from a reference[2] for $CH_3NH_3PbBr_3$ thin films coated with ALD alumina as 500 nm and the carrier effective lifetime is considered as 20 ns based on our TRPL experiment. Thus D=0.125 cm^2/s. The largest perovskite nanowire has the average diameter of 362 nm. With S = 37.2±20 cm/s, D/d=(0.125 cm^2/s)/(362x10^{-7} cm) =3453 cm/s. Therefore the assumption S $\ll$ D/d is valid.

Simulation of absorption and E-field distribution of nanowire array

The optical simulations on perovskite/alumina nanowires were performed using a commercial simulator based on the FDTD method (Lumerical, Inc) for nanowire arrays. The nanowires were considered as $CH_3NH_3PbBr_3$ cylinders with average diameter of 361.7, 208.2 and 150.4 nm and a pitch of 977, 771 and 684 nm respectively embedded in alumina. A plane wave light source with wavelength=450-600nm was placed at a vertical position of z=3.8 μm with downward propagation. The nanowire surface was fixed at z=4.8 μm, while the x and y directions fulfill periodic boundary conditions (BC). A perfectly matched layer BC was chosen for the z direction.

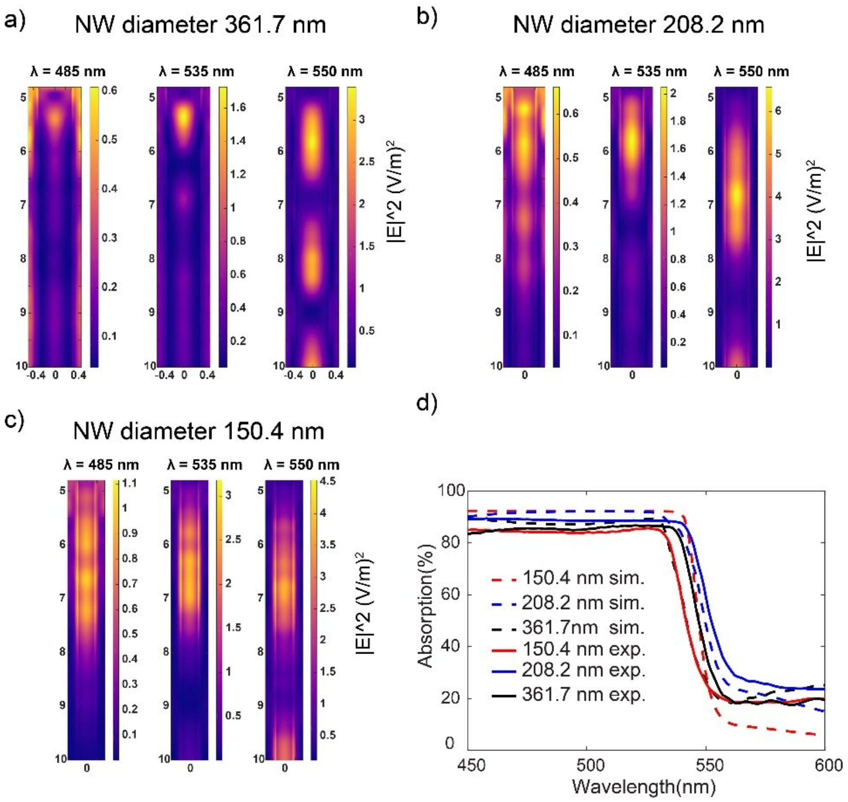

Figure S4. *The optical simulation of the electric field and absorption in perovskite/alumina nanowire arrays via FDTD simulations. a-c) |E|*^{2} *distribution at incident light wavelengths of 485, 535 and 550 nm for nanowires (NW) with different diameter as noted in the panels. 485 nm corresponds to the wavelength of the light excitation of the TRPL experiment, 535 nm to the perovskite bandgap and 550 nm to below band gap incident light. d) Simulated (dashed lines) and experimentally measured (solid lines) absorption spectra for nanowires. The below band gap absorption probably comes from from a slight tilt in sample mount during the experiment, and in the simulation from non-zero k optical constant of perovskite.*