Spatial and temporal imaging of long-range charge transport in perovskite thin films by ultrafast microscopy

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Charge carrier diffusion coefficient and length are important physical parameters for semiconducting materials. Long-range carrier diffusion in perovskite thin films has led to remarkable solar cell efficiencies; however, spatial and temporal mechanisms of charge transport remain unclear. Here we present a direct measurement of carrier transport in space and in time by mapping carrier density with simultaneous ultrafast time resolution and ~50-nm spatial precision in perovskite thin films using transient absorption microscopy. These results directly visualize long-range carrier transport of ~220 nm in 2 ns for solution-processed polycrystalline CH3NH3PbI3 thin films. Variations of the carrier diffusion coefficient at the μm length scale have been observed with values ranging between 0.05 and 0.08 cm² s⁻¹. The spatially and temporally resolved measurements reported here underscore the importance of the local morphology and establish an important first step towards discerning the underlying transport properties of perovskite materials.
ChARGE TRANSPORT IN SEMICONDUCTORS IS A CRUCIAL PROCESS THAT DEFINES EFFICIENCY FOR OPTOELECTRONIC DEVICES SUCH AS SOLAR CELLS AND LIGHT-EMITTING DIODES. SEMICONDUCTING ORGANIC–INORGANIC METAL HALIDE PEROVSKITES HAVE RECENTLY BEEN THE FOCUS OF INTENSE RESEARCH, MOTIVATED LARGELY BY THE RAPID RISE IN EFFICIENCY OF NEXT-GENERATION SOLAR CELLS BASED ON THESE MATERIALS. DEVELOPMENT OF PEROVSKITE SOLAR CELLS OVER THE PAST 5 YEARS HAS YIELDED CERTIFIED EFFICIENCIES AS HIGH AS 20.1%, SURPASSING THE PERFORMANCE OF LONG STANDING DYE SENSITIZED, ORGANIC AND AMORPHOUS SILICON PHOTOVOLTAIC TECHNOLOGIES1–10.

A WIDE RANGE OF OTHER APPLICATIONS UTILIZING LEADING HALIDE PEROVSKITES SUCH AS PHOTO- AND ELECTROCATALYTIC WATER SPLITTING ASSEMBLIES, OPTICALLY PUMPED LASERS, AND LIGHT-EMITTING DIODES HAVE ALSO BEEN RECENTLY DEMONSTRATED11–14.

THE EXCEPTIONAL CHARACTERISTICS OF HYBRID PEROVSKITES HAVE BROUGHT THEIR UNDERLYING OPTOELECTRONIC PROPERTIES UNDER HEAVY SCRUTINY, INCLUDING THE NATURE OF PHOTOGENERATED SPECIES AND THE EXCITED-STATE LIFETIME AND DECAY PATHWAYS15–18. OF THE VARIOUS PARAMETERS THAT DictATE PEROVSKITE DEVICE PERFORMANCE, THE CARRIER DIFFUSION LENGTH IS PARTICULARLY CRITICAL AS IT PROVIDES A BENCHMARK FOR OPTIMIZING DEVICE THICKNESS AND MORPHOLOGY. THE SUCCESS OF PEROVSKITE SOLAR CELLS HAS IN PART BEEN ATTRIBUTED TO LONG CARRIER LIFETIMES AND LONG-RANGE DIFFUSION ON THE ORDER OF 1 μM FOR BOTH ELECTRONS AND HOLES16,18–24. TO-DATE, SPECTROSCOPIC TECHNIQUES SUCH AS PHOTOLUMINESCENCE (PL) QUENCHING, TRANSIENT TERAZHZERT PHOTOCONDUCTIVITY AND TIME-RESOLVED MICROWAVE CONDUCTIVITY HAVE PRIMARILY BEEN UTILIZED TO INDIRECTLY ESTIMATE CARRIER DIFFUSION LENGTH (L) IN LEAD HALIDE PEROVSKITES16,18,19,25–27. HOWEVER, RESULTS OF THESE EXPERIMENTS HAVE BEEN INCONGRUENT, WITH DETERMINED L VALUES VARYING MORE THAN AN ORDER OF MAGNITUDE (100 nm–5 μm) IN PROTOTYPICAL METHYLAMMONIUM LEAD IODIDE (CH₃NH₃PbI₃) POLYCRYSTALLINE FILMS. THIS CAN IN PART BE ATTRIBUTED TO THE DIFFERENT EXCITED-STATE PROCESSES (RADIATIVE VERSUS NON-RADIATIVE RECOMBINATION) PROBED BY THE VARIOUS TECHNIQUES26. MOST RECENTLY, CARRIER DIFFUSION LENGTH OF >175 μM HAS BEEN MEASURED IN SINGLE CRYSTALS OF LEAD HALIDE PEROVSKITES, WHICH ESTABLISHES THE UPPER LIMIT FOR CARRIER TRANSPORT IN THESE MATERIALS28,29.

THESE DIVERGENT RESULTS ARE FURTHER CONVOLVED BY PREVIOUS STUDIES THAT REPORT LONGER ELECTRON AND HOLE DIFFUSION LENGTHS FOR THE MIXED HALIDE PEROVSKITE CH₃NH₃PbI₃–C₃Cl RELATIVE TO ITS TRIODIDE ANALOGUE16. NOTABLY, HOWEVER, CHLORINE HAS YET TO BE DETECTED IN THE FINAL MIXED HALIDE PEROVSKITE FILM30,31, SUGGESTING THAT ANY DISCREPANCIES IN ELECTRONIC PROPERTIES MAY STEM FROM MORPHOLOGICAL RATHER THAN COMPOSITIONAL DIFFERENCES. IN LIGHT OF THESE FINDINGS, IT IS EVIDENT THAT UNRAVELLING CHARGE DYNAMICS AND TRANSPORT MECHANISMS IS COMPLICATED BY THE COMPLEX AND HETEROGENEOUS NATURE OF HYBRID PEROVSKITE THIN FILMS, WHICH STRONGLY DEPENDS ON PROCESSING CONDITIONS AND PRECURSORS30,32. THE USE OF BULK OR ENSEMBLE SPECTROSCOPIC TECHNIQUES HINDERS RELIABLE DETERMINATION OF THE UNDERLYING MATERIAL PROPERTIES IN HYBRID PEROVSKITES.

ADDRESSING THESE CHALLENGES REQUIRES SPECTROSCOPIC TOOLS WITH HIGH SPATIAL RESOLUTION THAT ARE CAPABLE OF CAPTURING CHARGE DYNAMICS AND TRANSPORT AT THE SUBMICRON SCALE. THIS CAN BE ACHIEVED BY COMBINING MICROSCOPY TECHNIQUES WITH ULTRAFAST SPECTROSCOPIC METHODS33–35. PRIOR WORK USING ULTRAFAST ABSORPTION MICROSCOPY HAS BEEN USED TO STUDY DEACTIVATION PROCESS OF CH₃NH₃PbI₃ PEROVSKITE FILM36. PROBING CARRIER TRANSPORT AT THE LOCAL RATHER THAN ENSEMBLE LEVEL CAN CIRCUMVENT MANY OF THE INCONSISTENCIES THAT ARISE FROM PEROVSKITE SAMPLE PREPARATION. BECAUSE CARRIER SCATTERING AND RELAXATION PROCESSES ARE OFTEN ON THE SUB-NANOSECOND TIME SCALE, ULTRAFAST TIME RESOLUTION IS ALSO NECESSARY FOR ELUCIDATING THESE MECHANISMS.

HERE WE PRESENT DIRECT MEASUREMENT OF CARRIER TRANSPORT IN BOTH SPACE AND TIME BY MAPPING CARRIER DENSITY IN CH₃NH₃PbI₃ WITH SIMULTANEOUS FEMTOSECOND TIME RESOLUTION AND ~50-NM SPATIAL PRECISION USING ULTRAFAST ABSORPTION MICROSCOPY (TAM). USING THIS TECHNIQUE, LONG-RANGE CARRIER TRANSPORT HAS BEEN DIRECTLY VISUALIZED IN SOLUTION-PROCESSED CH₃NH₃PbI₃ THIN FILMS. WE SUCCESSFULLY MODEL SPATIAL AND TEMPORAL DEPENDENCE OF CHARGE DENSITY USING A DIFFUSION MODEL THAT INCLUDES HIGHER ORDER CARRIER RECOMBINATION PROCESSES. OUR MEASUREMENTS OF CARRIER CARRIERS IN POLYCRYSTALLINE CH₃NH₃PbI₃ THIN FILMS YIELD DIFFUSION CONSTANTS THAT IS TWO-TO EIGHTFOLD HIGHER THAN THOSE INFERRED FROM PREVIOUS BULK PL-QUENCHING MEASUREMENTS, POINTING TOWARDS THE IMPORTANCE OF LOCAL MORPHOLOGY IN CONTROLLING CARRIER TRANSPORT IN THE POLYCRYSTALLINE THIN FILMS.

RESULTS

STRUCTURAL AND OPTICAL CHARACTERIZATIONS. AN OPTICAL MICROGRAPH OF THE SPECIFIC AREA USED FOR TAM MEASUREMENTS REVEALS Crystalline CH₃NH₃PbI₃ ISLANDS ON GLASS SUBSTRATE (FIG. 1A). X-RAY DIFFRACTION PATTERN OF THE SAMPLE SHOWS SHARP AND STRONG PEROVSKITE (110) AND (220) PEAKS, INDICATING THAT CH₃NH₃PbI₃ FILM IS CRYSSTALLINE (SUPPLEMENTARY FIG. 1). SCANNING ELECTRON MICROSCOPY IMAGING OF THE SAMPLE MORPHOLOGY INDICATES THE FILM HAS GRAIN SIZE RANGING FROM ~100 TO 500 nm (FIG. 1B), THEREFORE, THE REGIONS OF INTEREST IN FIG. 1A IS NOT A SINGLE CRYSTAL BUT COMPOSED OF MULTIPLE CRYSTALINE DOMAINS. THE OPTICAL QUALITY OF THE PEROVSKITE THIN FILM WAS VERIFIED BY RECORDING THE ABSORPTION AND PL SPECTRA OF A ~500 nm × 500 nm SAMPLE AREA (FIG. 1C, LOWER PANEL). THE ABSORPTION AND PL SPECTRA FROM THIS LOCALIZED AREA CORRELATE WELL WITH THOSE OF BULK CH₃NH₃PbI₃, INDICATING THAT THIS REGION IS INDEED COMPOSED OF HIGH-Quality PEROVSKITE CRYSTALITES.

TO TRACK CHARGE–CARRIER DYNAMICS IN THE PEROVSKITE FILM, WE FIRST IDENTIFY TRANSIENT ABSORPTION SPECTRAL SIGNATURES FOR EXCITED CARRIERS. THE UPPER PANEL OF FIG. 1C SHOWS THE ENSEMBLE TRANSIENT ABSORPTION SPECTRA OF CH₃NH₃PbI₃. THERE ARE TWO DOMINANT PHOTOINDUCED-BLEACHING BANDS AT 480 AND 760 nm. THE PHOTOINDUCED-BLEACHING BAND AT ~760 nm CORRESPONDS TO THE BAND-EDGE ABSORPTION15,19. ASSIGNMENT OF THE 480-nm BAND AND THE BROAD PHOTOINDUCED ABSORPTION IS LESS OBVIOUS. A LOWER VALENCE BAND TO CONDUCTION BAND TRANSITION IN A TWO-VALENCE-BAND MODEL WAS FORMERLY PROPOSED TO EXPLAIN THE VARIOUS EXCITED-STATE SPECTRAL FEATURES37. THE HIGH-ENERGY FEATURES HAVE SINCE BEEN ATtributed TO AN IODIDE-TO-LEAD CHARGE TRANSFER TRANSITION THAT CAN ACOUNT FOR THE 480-nm BAND AND THE BROAD PHOTOINDUCED ABSORPTION SIGNALS37. HERE WE CHOOSE 580 nm AS THE PROBE WAVELENGTH FOR TAM MEASUREMENTS BECAUSE IT LIES NEAR THE CENTRE OF THE PHOTOINDUCED ABSORPTION SIGNAL (AWAY FROM ANY ISOSBESTIC POINT) AND IS FREE FROM THE SPECTRAL SHIFTS DUE TO THE PREVIOUSLY REPORTED BAND FILLING EFFECT AT HIGH PUMP INTENSITIES15.

THE TAM IMAGE OF THE INVESTIGATED REGION TAKEN AT 0-PS PUMP–PROBE DELAY IS SHOWN IN FIG. 1D. IN THIS MEASUREMENT, THE PUMP AND PROBE BEAMS OVERLAP IN SPACE AND THE TAM IMAGE REFLECTS THE MORPHOLOGY OF THE CH₃NH₃PbI₃ CRYSTALITE AS CAN BE SEEN FROM THE CORRESPONDENCE BETWEEN FIG. 1A,D. THE PUMP–PROBE TAM SIGNAL IN FIG. 1D IS PROPORTIONAL TO THE INITIAL DENSITY OF EXCITED CARRIERS AND HAS CONTRIBUTION FROM BOTH ELECTRONS AND HOLES. IT IS IMPORTANT TO NOTE THAT, UNLIKE PL-BASED EXPERIMENTS, TRANSIENT ABSORPTION IS CAPABLE OF MONITORING BOTH LUMINESCENT AND NON-LUMINESCENT SPECIES. THIS IMPORTANT DISTINCTION HAS BEEN NOTED AS A POTENTIAL CAUSE FOR THE UNDERESTIMATION OF DIFFUSION LENGTH IN PL STUDIES OF CH₃NH₃PbI₃12,26,38.

TAM IMAGING OF CARRIER TRANSPORT. TO IMAGE CARRIER TRANSPORT, A DIFFERENT MODALITY OF TAM IS EMPLOYED. THE PUMP BEAM IS FIXED AT A KNOWN POSITION, WHILE THE PROBE BEAM IS SCANNED RELATIVE TO...
the pump position with a Galvanometer scanner to form an image (for more details, see Methods and Supplementary Fig. 2). In such TAM images, spatial distribution of carrier density as a function of pump–probe delay can be directly visualized. At 0 ps, the TAM image represents the initial photogenerated carrier population created by the pump pulse. At later delay times, the TAM image reflects carrier diffusion away from the initial excitation volume. Figure 2 presents TAM images of carrier density at different pump–probe delay times. Carrier diffusion is represented by the evolution of the carrier distribution profile as time elapses. Note that the precision in the carrier propagation distance is dictated by the smallest measurable change in the excited-state population profile and is determined by signal-to-noise, rather than by the diffraction limit. By applying the megahertz frequency modulation on the pump beam, shot-noise-limited detection is achieved with our TAM setup with change of transmission ($\Delta T/T$) on the level of $5 \times 10^{-7}$ detectable. For the signal-to-noise levels shown in Fig. 2 and Fig. 3, this limit is $\sim 50$ nm in resolving diffusion (see Supplementary Note 1 for more details on detection limit).

We note here that the sample region being investigated in Figs 2 and 3 is optically flat and homogeneous. As quantitative evidence, the histogram analysis of signal distribution in the TAM images with spatially overlapped pump and probe beams is well described by a Gaussian function and the variance is in good agreement with the noise level of the measurements. 

Figure 1 | Structural and optical characterizations of CH$_3$NH$_3$PbI$_3$ perovskite film. (a) Optical micrograph of a microcrystalline region in a CH$_3$NH$_3$PbI$_3$ perovskite film. (b) Scanning electron micrograph (SEM) centred within a single representative perovskite flake. The scale bar is 0.5 $\mu$m. (c) Upper panel: transient absorbance spectrum measured at 50 ps in the bulk phase; lower panel: absorption and PL spectra of the sample region in (a). (d) Transient absorption imaging of the selected region of perovskite flake (dashed lines in (a)) at 0 ps. The whole image is $10 \times 10 \mu$m in size, with a scale bar of 1 $\mu$m.

Figure 2 | Two-dimensional transient absorption microscopy (TAM) imaging. The 2D imaging of the carrier density profile in CH$_3$NH$_3$PbI$_3$ at different pump-probe delay times. The initial carrier density was $4 \times 10^{18}$ cm$^{-3}$ at zero delay time. For delay time $>1$ ps, the signal maximum in each image was normalized to the signal maximum at 1 ps. The scale bar in the figure is 300 nm.
Modelling carrier transport in CH$_3$NH$_3$PbI$_3$. The charge diffusion process in the perovskite films in absence of an electric field is modelled as in-plane two-dimensional (2D) diffusion because the signal is integrated over the out-of-plane direction. The population decay rate includes 2D diffusion from the excitation volume, relaxation to the ground state as well as higher order recombination process. We use the following phenomenological diffusion model,

\[
\frac{\partial n(x, y, t)}{\partial t} = D \left[ \frac{\partial^2 n(x, y, t)}{\partial x^2} + \frac{\partial^2 n(x, y, t)}{\partial y^2} \right] - \frac{n(x, y, t)}{\tau} - \gamma n^2(x, y, t) - \eta n^3(x, y, t)
\]

where \(n(x, t)\) is the carrier population as a function of position and time, \(D\) is the diffusion constant assuming isotropic diffusion, \(\tau\) is the carrier lifetime, \(\gamma\) is the bimolecular recombination coefficient and \(\eta\) is the Auger recombination coefficient. Please note that \(\tau\) includes both response of electrons and holes and we assume them to have similar lifetimes.

The initial population \(n(x, y, 0)\) follows a 2D Gaussian distribution as created by a Gaussian pump beam at position \((x_0, y_0)\) (the pump beam profile is shown in Supplementary Fig. 4):

\[
\begin{align*}
n(x, y, 0) &= N_{exp} \exp\left(\frac{-(x-x_0)^2}{2\sigma_{0x}^2} - \frac{(y-y_0)^2}{2\sigma_{0y}^2}\right), \\
n(x, y, t) &= N_{exp} \exp\left(\frac{-(x-x_0)^2}{2\sigma_{tx}^2} - \frac{(y-y_0)^2}{2\sigma_{ty}^2}\right)
\end{align*}
\]

At low excitation intensity where the higher order recombination terms are negligible, the solution of equation (1) reduces into a 2D Gaussian distribution representing a spreading out population as a function of delay time \(t\). In equation (2), \(\sigma_{tx}^2\) and \(\sigma_{ty}^2\) are the time-dependent variances of the Gaussian profiles along \(x\) and \(y\) direction. Carrier diffusion length \(L\) at delay time \(t\) is related to the variance of the excited-state density profile \(\sigma^2\) by convolution rule (see Supplementary Note 2 for details). For instance, along the \(x\) axis,

\[
\sigma_{tx}^2 = \sigma_{0x}^2 + L^2 = \sigma_{0x}^2 + aDt
\]

The coefficient \(a\) is related to the dimensionality of the diffusion process. For 2D diffusion, \(a = 4\). Therefore, the diffusion constant \(D\) is then given by

\[
D = \frac{\sigma_{tx}^2(t) - \sigma_{tx}^2}{4t}
\]

Using equation (4) and results from the TAM experiments we can directly determine the diffusion coefficient for charge carriers in CH$_3$NH$_3$PbI$_3$.

To quantitatively model the excited-carrier diffusion, it is important to first perform the measurements at low fluence to minimize the influence of higher order recombination events and establish values for \(D\). This is supported by previous reports that demonstrate the CH$_3$NH$_3$PbI$_3$ excited-state decay proceeds primarily through first order processes at low carrier density$^{25}$. Because no apparent angular anisotropy was observed in the 2D imaging results (see Fig. 2), we performed one dimensional (1D) scans to reduce data redundancy and allow longer time integration for improved signal-to-noise ratio.

As shown in Fig. 3a, the normalized 1D profiles of carrier density exhibit a time-dependent broadening. Those profiles are well described by Gaussian functions within the instrument noise level. Figure 3b plots the Gaussian variation as a function of pump–probe delay time for four different locations on the CH$_3$NH$_3$PbI$_3$ thin film that are fitted to equation (3). The strong correlation between equation (3) and the experimental data suggests that carrier transport is diffusive in the low carrier density limit. The diffusion constant \(D\) measured at the four different locations ranges from 0.05 to 0.08 cm$^2$ s$^{-1}$.

To understand the spatial–temporal behaviour of charge transport, we modelled the carrier density as function of delay time and probe position using equation (1). The three-dimensional surface representing the temporal and spatial distribution of carriers is illustrated in Fig. 4a, which is simulated by numerically solving equation (1), taking into account convolution with the Gaussian profile of the probe beam (~230 nm, full-width at half maximum).

We determine \(\tau\) in our sample by fitting the kinetic traces to equation (1) under low carrier density. The result for an initial carrier density of $4 \times 10^{17}$ cm$^{-3}$ is shown in Fig. 4c. The diffusion model as described by equation (1) fits the dynamics taken at different pump–probe spatial separations very well as shown in Fig. 4c, which implies that the model is sufficient to
capture the carrier transport processes. The only part that is not captured by the model is the short-time decay (<200 ps) when pump and probe beams are overlapped in space (Fig. 4c, black trace). This fast relaxation probably comes from other excited-state complexes do not diffuse because the transient absorption signal includes excited-state absorption of all species, and not just free electrons and holes. One possible candidate for such excited-state complex is the CH$_3$NH$_3$PbI–I$_2$ charge transfer state$^{37}$. Free electrons and holes. One possible candidate for such excited-state complexes do not diffuse because the transient absorption distribution as a function of time and space is modelled at two set of parameters. As shown in Fig. 4c,d, the carrier density distribution as a function of time and space is modelled at two initial carrier densities, $4 \times 10^{17}$ cm$^{-3}$ and $4 \times 10^{18}$ cm$^{-3}$. The only fitting parameter that is varied between Fig. 4c,d is the initial carrier density $n(x,y,0)$. The resulting second and third order decay constants, are $\gamma = 6 \times 10^{10}$ cm$^{-3}$ s$^{-1}$ and $\eta = 10^{-27}$ cm$^6$ s$^{-1}$, respectively. The second order decay constant correlates well with previous values determined from time-resolved terahertz spectroscopy of CH$_3$NH$_3$PbI$_3$ thin films$^{25}$.

The simulated results of equation (1) in Fig. 4 also show that the higher order recombination terms have profound effects on transport. As an illustration, $\sigma_2^2(t) - \sigma_0^2(0)$ as a function of time delay at different initial carrier densities (1 $\mu$cm$^{-2}$ $2 \times 10^{17}$ cm$^{-3}$, 5 $\mu$ cm$^{-2}$ $10^{18}$ cm$^{-3}$) and 15 $\mu$ cm$^{-2}$ $3 \times 10^{18}$ cm$^{-3}$) is plotted in Fig. 4b. It is clear that $\sigma_2^2(t) - \sigma_0^2(0)$ grows linearly with delay time in the low carrier density limit. However, at high carrier densities, higher order terms make the broadening of the carrier diffusion artificially fast, suggesting that equations (2) and (3) are not valid at high-intensity excitation ($>1 \mu$ cm$^{-2}$) and the higher order recombination effects must be included to extract the right diffusion constants.

**Discussion**

The $D$ value measured in micron-sized regions of CH$_3$NH$_3$PbI$_3$ is as high as 0.08 cm$^2$s$^{-1}$, 2–8 times greater than previous estimates of $0.011–0.036$ cm$^2$s$^{-1}$ using PL-quenching measurements in
bulk polycrystalline perovskite thin films\textsuperscript{16,19}. This discrepancy most likely stems from unfavourable interactions at grain boundaries in bulk thin-film measurements. This is consistent with the very recent report on improving carrier mobility by enlarging grain size\textsuperscript{46}. As photogenerated charges diffuse through the solution-processed semiconductor film, they are more likely to be scattered by defects leading to a shorter lifetime \(\tau\) and smaller \(D\). This is also reflected in our own results that reveal the measured diffusion length can vary depending on location of the CH\(_3\)NH\(_3\)PbI\(_3\) film (Fig. 3b). By extrapolating the TAM results over the full excited-state lifetime at low fluence (\(\sim 50\) ns) and assuming a time-independent diffusion constant, we estimate a carrier diffusion length of \(\sim 1.2\) \(\mu\)m in polycrystalline CH\(_3\)NH\(_3\)PbI\(_3\).

We here compare our approach with other techniques. The charge diffusion in CH\(_3\)NH\(_3\)PbI\(_3\) polycrystalline films embedded in different architectures has been investigated using a variety of experimental techniques, including PL quenching, time domain terahertz and microwave photoconductance techniques\textsuperscript{16,18,19,25–27}. The charge mobility in mesoporous Al\(_2\)O\(_3/\)CH\(_3\)NH\(_3\)PbI\(_3\) film and vapor-deposited CH\(_3\)NH\(_3\)PbI\(_3/C\text{Cl}_2\) have been investigated by transient terahertz experiments\textsuperscript{25} on a similar time scale (nanoseconds) as this work, and has been determined to be on the same order but approximately 2.5–4 times higher than the values presented in this work. We attributed this discrepancy to two factors. First, the transient terahertz response reflects the sum of electrons and holes conductivities, while the transient absorption signal here gives an averaged value between the electrons and the holes depending on their absorption cross section at the probe wavelength. Second, sample fabrication details could also lead to different defect concentration that influences the carrier diffusivity. Solution processed Al\(_2\)O\(_3/\)CH\(_3\)NH\(_3\)PbI\(_3\) mesoporous film and vapor-deposited CH\(_3\)NH\(_3\)PbI\(_3/C\text{Cl}_2\) were used in ref. 25 and ref. 26, respectively, and we used solution-processed CH\(_3\)NH\(_3\)PbI\(_3\) film on glass. We note here that the carrier lifetime for our sample is 50–60 ns, which is shorter than other reported values\textsuperscript{41}. This could suggest a higher defect concentration in the film we measured, which could also lead to a smaller diffusion coefficient than what is reported in ref. 25. Transient microwave photoconductivity measurements\textsuperscript{18,27} have reported similar diffusion coefficient values (0.05–0.1 cm\(^2\) s\(^{-1}\)) in neat CH\(_3\)NH\(_3\)PbI\(_3\) perovskite film\textsuperscript{18}.

Our observations of spatial variation in carrier transport (Fig. 3b) underscore the importance of understanding the role of local morphology in dictating charge-carrier transport through organic–inorganic perovskites, and serve as a basis for further investigations into the relationship between structural order and diffusion in these materials. Very recently, measurements of carrier transport in large CH\(_3\)NH\(_3\)PbI\(_3\) perovskite single crystals revealed very long carrier lifetime and large diffusion length due to absence of grain boundaries and low defect concentration\textsuperscript{28,29,46}. The diffusion coefficients at the single crystal level can be as high as 0.52–0.99 cm\(^2\) s\(^{-1}\), which sets an upper limit for the mobility of free carriers generated in CH\(_3\)NH\(_3\)PbI\(_3\) perovskite structure.

It should be noted that even in the presence of grain boundaries, the diffusion coefficient only decrease by one order of magnitude compared with that in single crystal, much less of a decrease than other semiconductors such as silicon. Despite the inability to directly compare single crystal and thin-film results, grain boundaries and defect sites remain an important consideration in determination of transport properties in hybrid perovskites\textsuperscript{47,48}. Another salient result from our experiments is the diffusive transport of charge carriers in CH\(_3\)NH\(_3\)PbI\(_3\) over several nanoseconds. This implies trap states do not significantly influence transport on this time scale since trapping and detrapping of carriers would lead to subdiffusive behaviour\textsuperscript{35}. Trap states could become more important in limiting transport for the longer time scales. These transport properties support the exceptional functionality of polycrystalline organic–inorganic perovskites in optoelectronic device applications despite their low-energy processing requirements.

We interpret carrier transport in CH\(_3\)NH\(_3\)PbI\(_3\) using kinetic theory in semiconductors\textsuperscript{49}, where carrier transport is limited by carrier scattering.

\[
D = \frac{\mu kT}{q} = \frac{1}{m^*} \bar{\tau} kT = 3\sigma^2 \bar{\tau},
\]

Here \(m^*\) is the effective mass of the carriers, \(\mu\) is the carrier mobility, \(q\) is the carrier charge, \(\bar{\tau}\) is the average scattering time of the carriers, and \(v\) is root mean square velocity of the carrier, \(v = \sqrt{\frac{kT}{m^*}}\).

Electronic structure calculations on the CH\(_3\)NH\(_3\)PbI\(_3\) lattice suggest that both electrons and holes have a small effective mass between 0.2 and 0.3 times the free electron rest mass, \(m_0\) (ref. 50).

At room temperature (300 K), \(\bar{\tau}\) of CH\(_3\)NH\(_3\)PbI\(_3\) charge carriers is estimated to be \(\sim 0.28\) fs using a \(D\) value of 0.06 cm\(^2\) s\(^{-1}\) (average value from the four positions measured in our experiments), which is comparable to the scattering times in amorphous silicon (\(\sim 0.46\) fs)\textsuperscript{51}. The corresponding scattering length in the CH\(_3\)NH\(_3\)PbI\(_3\) structure is around 1 Å. \(\bar{\tau}\), in the subfemtosecond regime due to contributions from all possible scattering sources including phonons, defects and impurities, and is given by the sum of rates from all these processes\textsuperscript{52,53}. The short scattering length implies that strong scattering occurs primarily within the lattice. Considering that the nearest equilibrium distance of an iodine atom and methylammonium group is only about 2.6 Å in CH\(_3\)NH\(_3\)PbI\(_3\), it is very possible that the organic ligand acts as the scattering source for the charges carried by iodine and lead\textsuperscript{54}.

In summary, we present direct measurement of carrier transport in space and time by mapping carrier density in polycrystalline CH\(_3\)NH\(_3\)PbI\(_3\) thin films using transient absorption microscopy. Long-range carrier transport (\(\sim 220\) nm in 2 ns) has been directly visualized for solution-processed CH\(_3\)NH\(_3\)PbI\(_3\) films. We successfully model spatial and temporal dependence of charge density using a diffusion model and show that higher order carrier recombination processes have profound impact on transport. Our measurements yield diffusion coefficient as high as 0.08 cm\(^2\) s\(^{-1}\) and an extrapolated diffusion length of \(\sim 1.2\) μm over a lifetime of 50 ns. These values are significantly larger than those inferred from bulk PL-quenching experiments in similar polycrystalline CH\(_3\)NH\(_3\)PbI\(_3\) thin films.

The spatially and temporally resolved measurements reported here establish an important step towards discerning the underlying transport properties of hybrid perovskite materials. Most notably, parameters relevant for device applications, such as diffusion length and the impact of higher order recombination on carrier transport have been elucidated directly, minimizing the added complexity and variability associated with bulk thin-film samples. This provides strong evidence that the morphology of the various perovskite films heavily influences carrier transport. Therefore, we posit that CH\(_3\)NH\(_3\)PbI\(_3\) can exhibit comparable photovoltaic performance relative to CH\(_3\)NH\(_3\)PbI\(_3/C\text{Cl}_2\) in planar architectures provided the thin film is of sufficient quality. Direct determination of the transport properties in other hybrid perovskites using TAM will facilitate improved understanding of their properties. In addition, this technique can enable evaluation of the true photovoltaic potential of new materials without the variability associated with depositing contiguous, device-quality thin films.
Methods
Preparation of CH3NH3PbI3 perovskite film. Synthesis of methylammonium iodide (CH3NH3I) was carried out by dropwise addition of hydroiodic acid (57 wt%, aqueous, Alfa Aesar) into aqueous methylamine (40 wt%, Sigma Aldrich) under stirring at 0 °C for 2 h. The solvent was then removed by rotary evaporation and the crystals were washed in triplicate with diethyl ether and dried overnight under vacuum.

Equimolar quantities of PbI2 (99%, Acros Organics) and CH3NH3I were dissolved in N,N-dimethylformamide at 200 mg mL−1 to form the CH3NH3PbI3 precursor solution. The solution was heated to 70 °C and stirred for 1 h to ensure full solvation of the precursor components. Glass cover slips were cleaned by first sonicing in detergent solution followed by rinsing with deionized water and a second sonicing in ethan. The perovskite precursor solution was deposited on the clean glass substrates by spin coating at 2,000 rpm for 30 s. The films were then treated at 100 °C for 20 min to form CH3NH3PbI3. All preparation steps were carried out in a dry nitrogen atmosphere.

Optical measurements. The spun cast perovskite film was packaged by placing another microscope cover slip on top of the film forming a sandwich configuration and wash with isopropyl alcohol and ethanol along with sonication to prevent any degradation due to air and moisture exposure. All the packaging procedures were carried out in the glove box filled with nitrogen atmosphere. Ultraviolet-visible absorption spectra were taken on a home-built absorption microscope system. The white light source (Tungsren Halogen Lamp, model 780, Newport Inc.) was coupled into fibre optics and focused on the perovskite film (focal length of 100 × NA (numerical aperture) 0.95 objective lens (Olympus UM Plan Fl)), which resulted in a focused beam with its diffraction full- width at half maximum < 550 nm for the 400–850 nm spectral range. The transmitted light was detected by a charge-coupled device spectrometer (LR1, AQeis instruments). The reference spectra were taken on a bare area on the same substrate.

The setup used for transient absorption measurements of the bulk CH3NH3PbI3 perovskite sample has been described before5. For the TAM measurements, a schematic layout of the optical setup has been included in Supplementary Fig. 2 and is also described in previous publications5,32. Briefly, a Ti: Sapphire oscillator (Coherent Mira 900) pumped by a Nd:YAG laser was adopted as the light source (output at 785 nm, 80 MHz repetition rate). 70% of the pulse energy was fed into the optical parametric oscillator (Coherent Mira OPO) to generate probe light at 580 nm, while the remainder 30% was doubled to 387 nm and serves as the pump beam. The repetition rate of both beams was reduced to 2.5 MHz using two clock-synchronized pulse pickers (Model 9200, Coherent Inc.). The pump beam was modulated at 1 MHz using an acoustic optical modulator (model R21080-1DM, Gooch&Housego). A 60 × NA = 1.49 objective (CFI Apo TIRF, Nikon Inc.) was used to focus the laser beams onto the sample, and the transmitted light was then collected by another objective (60 × NA = 0.9) and detected by an avalanche photodiode (Hamamatsu C5331-04). For morphological TAM imaging, pump beam and probe beam were overlapped spatially and a piezo electric stage (P-527.3CL, Physik Instrument) was used to scan the sample to construct images such as Fig. 1b. In charge diffusion imaging as shown in Figs 2 and 3, the pump beam was fixed, while the probe beam was scanned by a pair of Galvanometer mirrors (Thorlabs Inc.). The sensitivity of TAM method utilized to extract the diffusion coefficient in the carrier diffusion process is determined not by optical diffraction limit but by signal-to-noise level of the TAM measurements. A detailed analysis can be found in the Supplementary Note 1.

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Author contributions
L.H. and P.K. and Z.G. designed the experiments. Z.G. and J.M. and Y.W. carried out the measurements. Z.G and L.H analysed and modelled the data. Z.G and L.H wrote the manuscript.

Additional information
The authors declare no competing financial interests.

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