

Temperature and Gate Dependence of Carrier Diffusion in Single Crystal Methylammonium Lead Iodide Perovskite Microstructures

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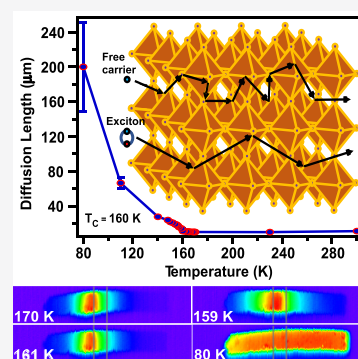
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ABSTRACT: We investigate temperature-dependent photogenerated carrier diffusion in single-crystal methylammonium lead iodide microstructures via scanning photocurrent microscopy. Carrier diffusion lengths increased abruptly across the tetragonal to orthorhombic phase transition and reached $200 \pm 50 \mu\text{m}$ at 80 K. In combination with the microsecond carrier lifetime measured by a transient photocurrent method, an enormous carrier mobility value of $3 \times 10^4 \text{ cm}^2/\text{V s}$ was extracted at 80 K. The observed highly nonlocal photocurrent and the rapid increase of the carrier diffusion length at low temperatures can be understood by the formation and efficient transport of free excitons in the orthorhombic phase as a result of reduced optical phonon scattering due to the dipolar nature of the excitons. Carrier diffusion lengths were tuned by a factor of 8 by gate voltage and increased with increasing majority carrier (electron) concentration, consistent with the exciton model.



Halide perovskites exhibit ideal electronic properties, including a long carrier lifetime and diffusion length, which are essential to their key involvement in the unprecedented rapid advancement in photovoltaic performance. While several mechanisms such as local polar fluctuation,¹ polaron formation,² spin–orbit coupling,³ ion migration,⁴ and ferroelectricity⁵ have been proposed, the true origins of these properties are still under intense debate. Exploration of these materials at low temperatures reduces complications resulting from thermal fluctuations. Carrier mobilities are shown to follow a power law dependence on temperature ($\mu \propto T^{-1.5}$) in both methylammonium lead iodide (MAPbI₃)^{6,7} and bromide (MAPbBr₃),⁸ consistent with phonon scattering experiments.^{9–13} Along with mobility, charge carrier diffusion length L_{diff} is a critical optoelectronic parameter, determined by the diffusion coefficient D and the lifetime τ of the charge carriers, related by the expression $L_{diff} = \sqrt{D\tau}$, and D is related to the carrier mobility by $\mu = qD/k_B T$. L_{diff} values have been experimentally determined by separately measuring μ and τ ^{14,15} or determined directly from spatially resolved photoluminescence¹⁶ or photocurrent measurements.^{17–20}

Here, we examine the roles that the temperature and structural phase play in carrier transport and recombination within MAPbI₃ single crystal microstructures. We apply scanning photocurrent microscopy (SPCM) to directly extract the carrier diffusion length in MAPbI₃ microplate field effect transistors (FETs) in the temperature range of 80–300 K. Studying single crystal halide perovskites eliminates the complications caused by grain boundaries that are present in

polycrystals. Furthermore, unlike bulk single crystals, single crystal nano- and microstructures²¹ allow in situ gate tuning of the Fermi level in the material,²² facilitating exploration of charge transport mechanisms. The single crystalline microstructures of MAPbI₃ are synthesized following a dissolution and recrystallization process.²³ Microbeams and microplates with a thickness of about 1–2 μm and length of up to 100 μm are produced with well-defined facets and smooth surfaces (Figure 1a). These microstructures are mechanically transferred to prepatterned Cr/Au electrodes on SiO₂-coated Si substrates to fabricate FETs. Such a direct transfer method avoids exposure of the sample to detrimental solvent processing as in a conventional lithographic process.

Under global illumination, the current first increases with source-drain bias (V_{SD}) then saturates as V_{SD} increases above 0.3 V (Figure 1b). The I – V_{SD} characteristics can be understood by a back-to-back diode model.²⁴ The saturation current changes abruptly at 147 and 156 K during cooling and warming, respectively (Figure 1c). The photocurrent change shows a single step and occurs in only a few milliseconds (Figures S2 and S3 in Supporting Information), implying that the entire sample undergoes phase transition simultaneously without any mixed phase domains. This critical temperature T_c agrees well with the reported values for the tetragonal to

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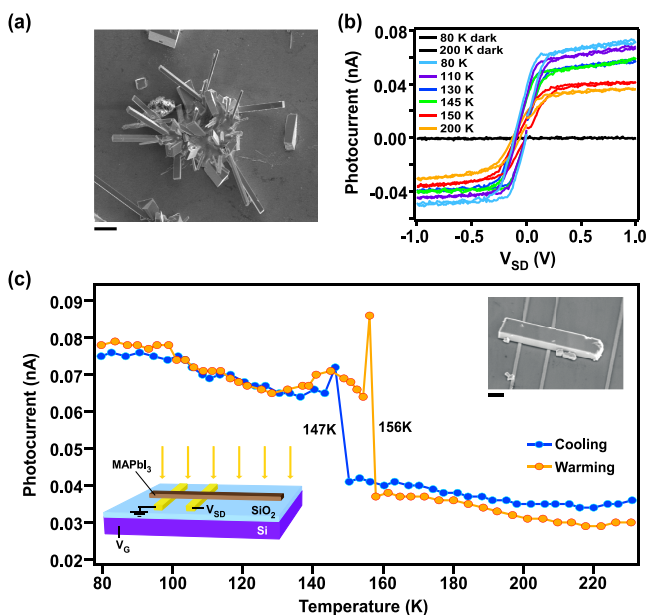


Figure 1. Photocurrent response across phase transition under global illumination. (a) Scanning electron microscopic (SEM) image of as-grown MAPbI₃ microcrystals. Scale bar represents 20 μm . (b) I - V_{SD} curves at various temperatures in the dark and under $5 \times 10^{-4} \text{ W/cm}^2$ global illumination. (c) Saturation photocurrent as a function of temperature with $V_{SD} = 1 \text{ V}$ and global illumination. The sample temperature is ramped slowly (3 K/min). Inset: left, schematic of a MAPbI₃ microplate FET under global illumination; right, SEM image of microplate device. Scale bar represents 5 μm .

orthorhombic phase transition.^{18,25} The specific T_c values vary from device to device in a range of 15 K among the 10 devices

we have measured to date and are lower in thinner samples, as noticed in a previous work.²⁵ Interestingly, we have occasionally observed a temporary photocurrent overshoot that occurs at the phase transition (Figure 1c), which may be related to the induced strain as the sample abruptly shrinks by 1% from the tetragonal to orthorhombic phase.²⁶

SPCM is then performed to extract carrier diffusion lengths.^{17,18,20,24,27,28} The experimental setup is displayed in Figure 2b, where a microplate device is locally excited by a focused 532 nm CW laser with a diameter about 1 μm . While the laser is raster scanned across the entire device surface, the photoinduced current is recorded as a function of laser position and then plotted into 2D photocurrent maps (Figure 2a). At $V_{SD} = 0 \text{ V}$, only very weak photocurrent is observed. At $V_{SD} = 3 \text{ V}$, the enhanced band bending at the reversely biased contact leads to a much stronger photocurrent (Figure S4). The photocurrent is peaked near the negatively biased contact, indicating the material is n -type.

While the maximum external quantum efficiency (EQE, defined by the number of collected electrons over the number of incident photons) remains about 35% at all temperatures, the photoresponse area sensitively depends on temperature. The laser generates photocurrent both inside and outside the channel, illustrating that the photoexcited carriers can diffuse from outside the channel to the electrodes. Above T_c , the photocurrent is only pronounced in the vicinity of the contacts. Below T_c , the active area in which laser can create photocurrent increases abruptly, which provides a microscopic understanding of the observed sudden photocurrent change under uniform illumination. At 80 K, the photocurrent remains nearly the same when the laser is scanned over the entire 90 μm long sample (Figure 2a and d), indicating that the locally

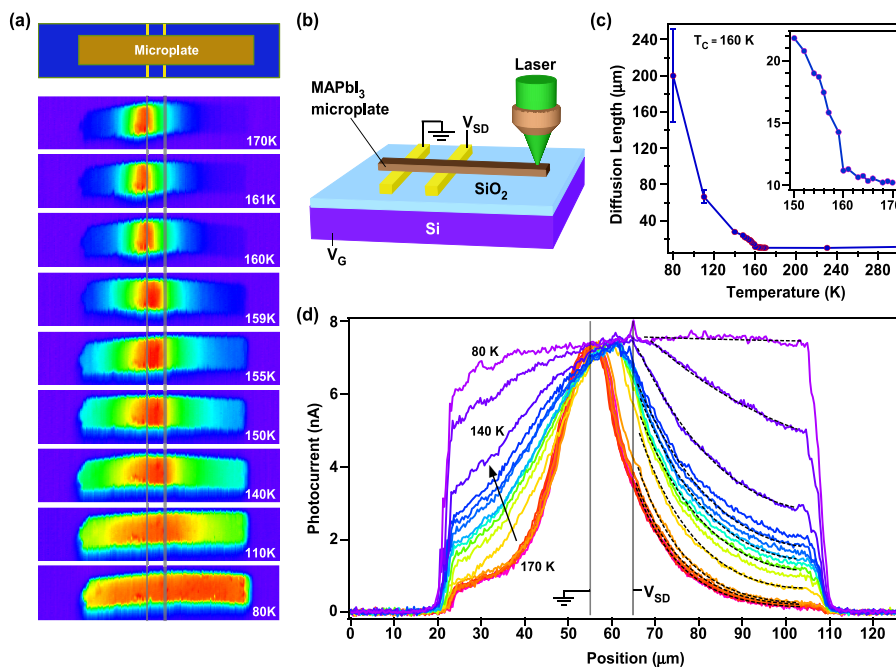


Figure 2. Spatially resolved photocurrent. (a) Device layout and photocurrent maps at various temperatures. Gray lines indicate electrode placement. (b) SPCM schematic. (c) Temperature-dependent carrier diffusion length extracted by curve fitting photocurrent distributions in (d). Inset shows zoomed-in view of values in the vicinity of T_c (160 K). (d) Photocurrent profiles along the microplate axis at various temperatures, taken during the warming process with a 50 nW laser power and $V_{SD} = 3 \text{ V}$. Gray vertical lines indicate electrode placement, and black dashed curves are curve fittings.

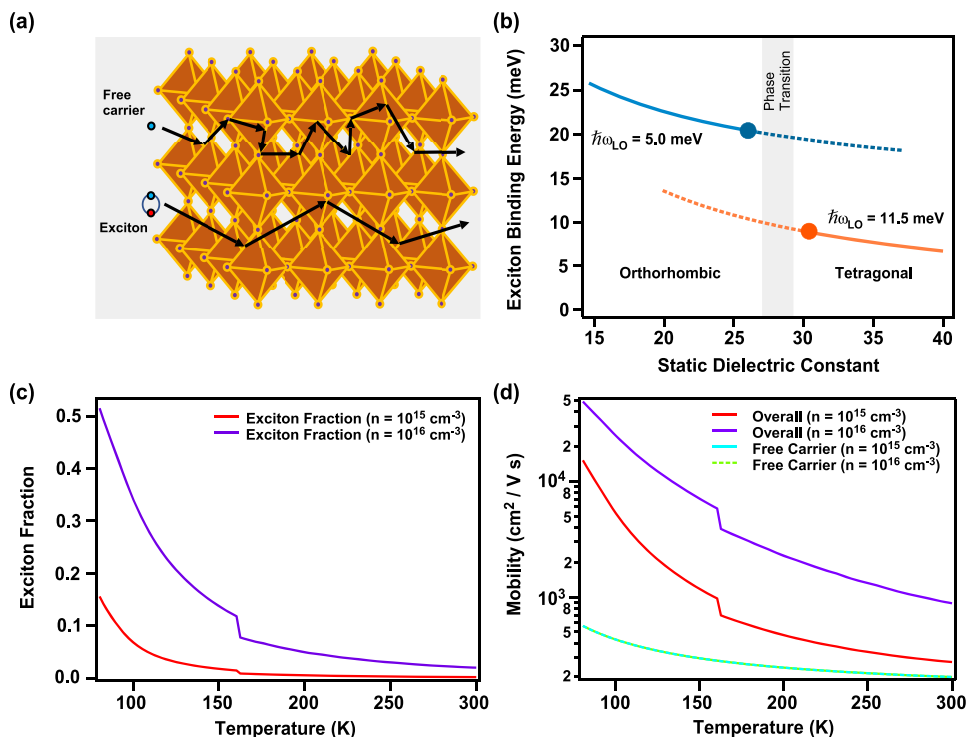


Figure 3. Calculation of free exciton and free carrier mobilities. (a) Visualization of free carrier versus exciton scattering in halide perovskites (scattering lengths not to scale). (b) Exciton binding energy, calculated by taking into account polaronic effects, as a function of the static dielectric constant and LO phonon frequencies, which are phase-dependent. (c) Calculated exciton fraction as a function of temperature, at carrier densities $n = 10^{15} \text{ cm}^{-3}$ and $n = 10^{16} \text{ cm}^{-3}$, showing significant exciton population at low temperatures. (d) Calculated free carrier mobility and overall mobility as a function of temperature. Free carrier mobility is independent of carrier density, while overall mobility is increased at higher densities due to higher exciton fractions.

generated carriers are equally capable of reaching the contacts and being collected, regardless of initial generation position.

Quantitatively, we extract photocurrent decay length L_D by fitting the photocurrent distributions along the microplate axis with a hyperbolic function $I(x_0) = I_0 \cosh[(x_0 - L)/L_D]$, where x_0 is the distance between the laser position and the contact and L is the length of the microplate outside the channel. A cosh function is used instead of exponential when L_D is not small compared with L ²⁹ (see math justification in the Supporting Information). We only fit the photocurrent distribution outside the channel to ensure diffusive transport of carriers¹⁷ and determine L_{diff} from L_D . L_D values are similar on both sides of the channel, and the slight difference is presumably caused by the variation in local defect density along the microplate. To rigorously confirm the accuracy of this method, we have simulated the photocurrent distributions by performing a 2D cross-sectional modeling of perovskite devices under local photoexcitation using COMSOL Multiphysics.²⁴ The simulated photocurrent distributions follow nicely the experimental data (Figure S5). The fits using a cosh function yield L_D in excellent agreement with L_{diff} calculated from the simulation parameters (Figure S5b).

The extracted L_D values remain about $10 \mu\text{m}$ above T_c but rapidly increase to $22 \mu\text{m}$ as the temperature decreases within 10 K below T_c (Figure 2c inset). At 80 K, L_D reaches $200 \pm 50 \mu\text{m}$. The large error bar at 80 K arises because of the finite sample length ($L < L_D$, see error analysis in the Supporting Information). L_D values at 80 K range from 100–200 μm depending on the sample (data for another sample is shown in Figure S6). Our result is different from a previous work,¹⁸

where the hole diffusion length was found to be at maximum $150 \mu\text{m}$ at 160 K but found to decrease to $50 \mu\text{m}$ at 96 K. The reason for this discrepancy is unclear but is most likely related to sample preparation. Our growth method yields samples with an exceptionally low trap density, as demonstrated previously.^{21,30–32}

Transient photocurrent measurements are then performed to obtain a carrier lifetime at various temperatures (Figure S7 and Methods). The carrier lifetime increases from less than 0.5 μs (our temporal resolution limit) above T_c to about 2 μs at 80 K for the same device used in Figure 2. From this lifetime and the measured L_{diff} we estimate a carrier mobility ($\mu = qL_{diff}^2/\tau k_B T$) of $3 \times 10^4 \text{ cm}^2/\text{V s}$ at 80 K, which is 1 order of magnitude higher than the highest reported values^{33,34} (Table S1). Lifetimes differ slightly across devices, ranging from <0.5 to 2 μs at 80 K (see the diffusion length and lifetime measurements acquired from another device in Figure S7b and d), but the mobility values are consistently high, on the order of 10^4 – $10^5 \text{ cm}^2/\text{V s}$ at 80 K.

The observed highly nonlocal photocurrent indicates the efficient transport of photogenerated charge carriers, which can generally be understood by four possible mechanisms: (a) photon recycling, (b) exciton polariton condensation, (c) free charge carrier diffusion, and (d) free exciton diffusion. We show that the first three mechanisms are unlikely. (a) Photon recycling via re-absorption/re-emission³⁵ is unlikely to account for the observed 200 μm photocurrent decay, as the optical loss through the light escaping the microplate surfaces alone would result in a maximum of 20 μm decay length according to our calculation (see Supporting Information), even when

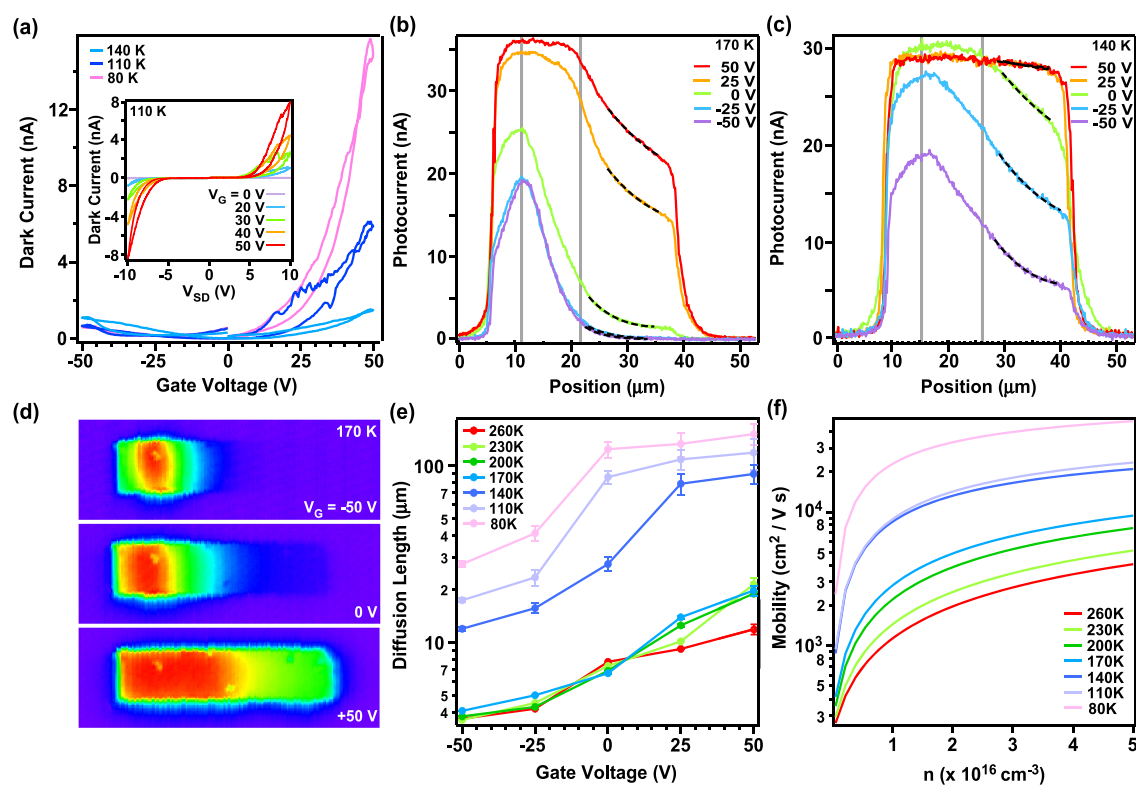


Figure 4. Field effect on carrier diffusion. (a) Dark current as a function of V_G at fixed $V_{SD} = 10$ V and various temperatures. Inset: Dark $I - V_{SD}$ curves at various V_G at 110 K. (b) and (c) show SPCM profiles with varying gate voltage and fixed bias of 1.5 V at 170 K (tetragonal phase) and 140 K (orthorhombic phase), respectively. Gray vertical lines indicate electrode placement. (d) Normalized photocurrent maps showing diffusion enhancement (suppression) at positive (negative) gate voltage at 170 K. (e) Carrier diffusion length at various temperatures as a function of gate voltage. (f) Simulated mobility values as a function of overall carrier density at various temperatures.

assuming unity photoluminescence efficiency. (b) Exciton polariton condensation³⁶ requires a microcavity structure to confine the light. Our microplate does not have such a structure and optical loss would result in a short decay length. Free minority carrier diffusion, mechanism (c), appears plausible but demands a 400-fold increase in mobility to account for the rapid increase of L_D below T_c from 160 to 80 K. Our molecular dynamics simulations of electron–phonon interactions and carrier effective masses (Supporting Information) show that this is inconsistent with the scaling expected for free carriers or charged polarons across the temperature range. Similarly, existing polaron models predict $\mu \propto T^{-1.5}$ and a mobility change of only a factor of 3 from 160 to 80 K.¹²

The above consideration leads us to attribute the origin of the highly nonlocal photocurrent at low temperatures to efficient exciton transport, mechanism (d). A relatively large value of the exciton binding energy E_b (larger than 20 meV) in the orthorhombic phase discontinuously drops to below 10 meV at room temperature in the tetragonal phase.³⁷ This is fairly consistent with the value of 16 ± 2 meV found in the orthorhombic phase and a few meV in the tetragonal phase in MAPbI₃ by magnetic field-dependent optical absorption.³⁸ Using an effective-interaction-potential model^{39,40} (Supporting Information), we calculated the exciton binding energies of MAPbI₃ in good agreement with the measurements, 20.1 and 9.1 meV in the low and high temperature phases, respectively, as shown in Figure 3b. These excitonic binding energies suggest that excitons are unlikely to form at room temperature but they become significant at low temperatures. The exciton fraction over the total carriers is shown in Figure 3c, calculated

following the approach used in a previous report⁴¹ and using the temperature-dependent exciton binding energy.³⁷ The abrupt increase in the exciton fraction across the phase transition is a result of phase-dependent exciton binding energies. Note that the exciton fraction sensitively depends on the total carrier density, as a high carrier density promotes exciton formation. The total carrier density in our sample is on the order of 10^{15} – 10^{16} cm⁻³, estimated from the laser power and carrier lifetime.

The rapid increase of the mobility at low temperatures can then be understood as the exponential increase of the exciton fraction with decreasing temperature. In this exciton model, the record-high mobility indicated by the long L_D does not contradict the nonexcitonic free carrier mobilities reported by earlier works. Even though an exciton is charge neutral, its mobility can be defined from its diffusion coefficient in analogy to charge by the Einstein relation: $\mu = qD/k_B T$. Charge neutral excitons create photocurrent when electron and hole pairs are separated as a result of band bending near the contact.

We hypothesize that the reason for the highly efficient exciton transport is the dipolar nature of excitons. Since dipole fields are shorter ranged than monopole fields, longitudinal optical (LO) phonons interact significantly less with excitons than with free carriers. Moreover, static ground-state excitonic dipoles do not exist in the centrosymmetric orthorhombic phases, and they can only be dynamically induced by other charge fluctuations such as LO phonons. As a result, the scattering of excitons is expected to be less frequent than that of free carriers or charged polarons. To estimate the relative scattering rates of free carriers and excitons, we consider the

interaction strength of an induced excitonic dipole, given by the polarizability of an exciton within a hydrogenic model with LO phonon charge fluctuations: $\alpha = \frac{18a_0^3}{4}$.⁴² Here, a_0 is the exciton Bohr radius. Compared to the interaction between free carriers (holes) and LO phonons, we find that the exciton–LO phonon interaction strength, or probability amplitude for scattering, is reduced by a factor of $\sqrt{\gamma} = \left(\frac{\alpha}{\epsilon_\infty R_x^4}\right) / \left(\frac{1}{R_h}\right)$.

Here, $R_h = \sqrt{\frac{\hbar}{2m_h\omega_{LO}}}$ and $R_x = \sqrt{\frac{\hbar}{2m_x\omega_{LO}}}$ are the hole and exciton polaron radii, respectively, that characterize the length scales of LO fluctuations around these species, with masses m_h and m_x , respectively. The scattering rate, or probability, is therefore reduced by a factor of $\gamma = \left(\frac{18a_0^3 R_h}{4\epsilon_\infty R_x^4}\right)^2$. Using typical values for MAPbI₃ (see Supporting Information), we find that the exciton scattering from LO phonons is reduced by a factor of $\gamma = 5 \times 10^{-4}$. This is a lower bound for γ , as other scattering mechanisms could be present for excitons. In Figure 3d, we plot the overall mobility, weighted by free carrier and excitonic contributions. The free-carrier mobility is calculated using the Kadanoff mobility,¹² while the exciton mobility was taken to be larger by a factor of $1/\gamma$. In Figure 3d, we show that the reduced excitonic scattering at a value of $\gamma = 6 \times 10^{-3}$ leads to increases in low-temperature mobility, comparable to the measured values in our devices.

Finally, we present the field effect on carrier diffusion in halide perovskite microplate FETs. In the dark, the conductance increases at positive V_G values, indicating the device is n -type (Figures 4a and S8). The gate dependence shows significant hysteresis at room temperature, as explained by gate-induced ion migration.²² The hysteresis is greatly reduced at lower temperatures, as ion migration is suppressed. By assuming a parallel plate capacitance (a combination of vacuum gap and oxide layer), an apparent field-effect mobility on the order of $0.01 \text{ cm}^2/\text{V s}$ can be extracted from the gate dependence at 80 K (Figure 4a). This apparent mobility value does not represent the real carrier mobility of the material because of large contact barriers evidenced by the nonlinear I – V_{SD} curves (Figure 4a inset and Figure S9). Furthermore, this low mobility value does not contradict the high mobility value indicated by the long photocurrent decay length, as the gate dependence measures the mobility for free carriers or charged polarons rather than excitons.

Photocurrent distributions sensitively depend on V_G (Figure 4b–d). At positive V_G , the photocurrent magnitude increases, likely caused by the reduced sample resistance and/or enhanced band bending at contact. The carrier diffusion length also significantly depends on the gate voltage, changing by a factor of 8 at low temperature as V_G varies from -50 to 50 V (Figure 4e). Such a strong electric field control of the carrier diffusion has not been reported before in halide perovskites. We consistently observe that L_D increases and decreases at positive and negative V_G , respectively. In the n -type device, this trend indicates that increasing the majority carrier (electron) concentration enhances the diffusion of the minority carrier (hole) or exciton. This behavior cannot be understood by the lifetime reduction at high majority carrier density as in other semiconductor nanodevices.^{43,44} Instead, this unusual gate dependence is consistent with the exciton model. The higher carrier concentration at positive V_G increases the probability of exciton formation, leading to a larger exciton fraction and,

hence, higher overall mobility (Figure 3). The calculated mobility values, taking into account exciton formation (Figure 4f), follow well the general trend of the experimental results.

In summary, we have observed temperature- and gate-dependent carrier diffusion in single-crystal MAPbI₃ microstructures. L_D remains about $10 \mu\text{m}$ in the tetragonal phase but increases sharply to $200 \mu\text{m}$ at 80 K in the orthorhombic phase. L_D also increases with the majority carrier (electron) concentration tuned by the gate voltage. The rapid increase of L_D can be understood by the formation and efficient transport of excitons at low temperature. The phonon-scattering rate of excitons is significantly suppressed as a consequence of their dipolar nature, compared to free carriers and charged polarons. This hypothesis is supported by calculated temperature- and carrier concentration-dependent mobilities that are in excellent agreement with the experimental results. Although the relatively low excitonic binding energy in MAPbI₃ suggests that excitonic effects only become important at low temperature in this material, excitons are expected to play a significant role at room temperature in low dimensional halide perovskites.^{45,46} Our work provides valuable insight for understanding the interplay among free carriers, excitons, and phonons in halide perovskite materials.

EXPERIMENTAL SECTION

Microstructure Growth and Device Fabrication. 40 mg of MAI powder (Sigma-Aldrich, >98%) was slowly dissolved in 1 mL of isopropyl alcohol (IPA, 99.5%) in a glass vial inside a nitrogen glovebox. Meanwhile 100 mg of PbAc₂·3H₂O (Sigma-Aldrich, 99.999%) powder was dissolved in 1 mL of deionized water. The PbAc₂ solution was distributed across the FTO-coated glass slides by spin-coating at 600 rpm for 40 s. The coated substrate was baked at 60 °C until dry and then placed upside down inside the vial of MAI solution at 50 °C for several days. Afterward, the substrate was gently dipped into IPA for a few seconds and then blown dry with nitrogen. The as-grown microstructures were then mechanically transferred via a microfiber to 300 nm SiO₂-covered Si substrates with prepatterned 10 nm Cr/30 nm Au electrodes to achieve single microplate FETs.

Optoelectronic Measurements. All measurements were performed in an optical cryostat (Janis ST-500) with a pressure of 10^{-6} Torr. Current–voltage curves were measured through a current preamplifier (DL Instruments, model 1211) and a NI data acquisition system. SPCM measurements were performed using a home-built setup based upon an Olympus microscope. A 532 nm CW laser was focused by a 40× objective lens to a diffraction limited spot of about $1 \mu\text{m}$ and raster scanned on a planar microstructure device by a pair of mirrors mounted on galvanometers to produce 2D photocurrent maps. For transient photocurrent measurements, we used a photoelastic modulator (Figure S7a) to modulate the light intensity at 50 kHz with a light intensity decay time about $0.5 \mu\text{s}$ (see more in the Supporting Information).

Electronic Structure Dynamics Calculations. We investigate the effect of temperature-dependent band structure fluctuations on free carrier mobility using simulations of atomic and electronic structure dynamics. Atomic motion is simulated using classical molecular dynamics (MD) with a force field by Mattoni et al.⁴⁷ at 10 temperatures between 100 and 300 K. Atomic positions are extracted every 30 fs over a 30 ps trajectory and used to calculate the electronic structure using a modified version of the tight-binding model by Mayers et al.,¹³ in which on-site

orbital energies are modified using both the Coulomb potential and its second derivative.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcllett.9b03643>.

Analytic justification of SPCM extraction of the carrier diffusion length by SPCM, COMSOL device simulation for SPCM profiles, error analysis, data on abrupt photocurrent change across the phase transition, band bending diagrams and bias-dependent SPCM results, temperature-dependent SPCM results in a different device, transient photocurrent measurement setup and results, gate-dependent dark conductance at various temperatures, estimation of photocurrent decay length via photon recycling, MD simulation approach and results, calculation of exciton binding energies, and X-ray diffraction data for MAPbI₃ microstructures (PDF)

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Notes

The authors declare no competing financial interest.

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