Photodriven Dipole Reordering: Key to Carrier Separation in Metalorganic Halide Perovskites

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ABSTRACT: Photodriven dipole reordering of the intercalated organic molecules in halide perovskites has been suggested to be a critical degree of freedom, potentially affecting physical properties, device performance, and stability of hybrid perovskite-based optoelectronic devices. However, thus far a direct atomically resolved dipole mapping under device operation condition, that is, illumination, is lacking. Here, we map simultaneously the molecule dipole orientation pattern and the electrostatic potential with atomic resolution using photoexcited cross-sectional scanning tunneling microscopy and spectroscopy. Our experimental observations demonstrate that a photodriven molecule dipole reordering, initiated by a photoexcited separation of electron–hole pairs in spatially displaced orbitals, leads to a fundamental reshaping of the potential landscape in halide perovskites, creating separate one-dimensional transport channels for holes and electrons. We anticipate that analogous light-induced polarization order transitions occur in bulk and are at the origin of the extraordinary efficiencies of organometal halide perovskite-based solar cells as well as could reconcile apparently contradictory materials’ properties.

KEYWORDS: organometal halide perovskites, scanning tunneling microscopy/spectroscopy, photodriven dipole reordering, electrostatic potential, one-dimensional carrier transport channels, light-induced polarization order transitions

In the search for the most economical yet still highly efficient solar cell material, halide perovskites developed rapidly toward the materials of choice due to their rather inexpensive production costs on almost any substrate, combined with power conversion efficiencies reaching over 20%. The success of halide perovskites has been suggested to stem from their surprising materials properties, that is, large carrier lifetimes and long diffusion lengths, leading to low carrier recombination rates as well as high absorption. The elucidation of the physical origins of these notable properties and conversion efficiencies led to an exceptionally intense research activity and the suggestion of different competing physical mechanisms. For example, theoretical calculations predict that the relative orientations of the intercalated CH₃NH₃⁺ (methylammonium, MA) organic molecule cations are critical for understanding the carrier conduction. Since these organic cations exhibit a polarization, their orientation is expected to induce local potential fluctuations and lead to random ferroelectric domains walls. Interestingly, ordered ferroelectric domain walls are predicted to induce potential fluctuations, separating the localization of holes and electrons, thereby reducing carrier recombination. Other
calculations suggest in contrast that the tilting/distortion of the octahedrons induces a localization of carriers\textsuperscript{12,17} and changes of the band gap.\textsuperscript{16,17} Although several previous works emphasize the important role of organic cation dipole’s orientation on the charge carrier separation, the only indirect experimental result stems from neutron scattering and suggests that the rotation of the MA organic molecule cation affects the electrical conductance.\textsuperscript{18}

Furthermore, understanding organometal halide perovskites in actual operating devices requires investigations under illumination.\textsuperscript{19–22} Such studies are highly critical in view of the recent observation of a light-induced giant dielectric constant\textsuperscript{23–25} and prediction of switching of (macroscopic) ferroelectric domains.\textsuperscript{26,27} These effects may be related to a light-induced reordering of the MA organic molecule cations and thermalization of carriers,\textsuperscript{26,28} but thus far there is no direct real-space microscopic experimental proof of any of these theories. Previous microscopic approaches by scanning tunneling microscopy lack a mapping of the potential landscape and, more importantly, provide no atomically resolved investigation under simultaneous illumination.\textsuperscript{29,30}

In this work, we use cross-sectional scanning tunneling microscopy (XSTM) and spectroscopy (XSTS) to study fundamental illumination-induced physical effects in methylammonium lead bromide perovskites (CH\textsubscript{3}NH\textsubscript{3}PbBr\textsubscript{3}, also referred to as MAPbBr\textsubscript{3}) single crystals, cleaved in ultrahigh vacuum, under simultaneous light illumination with atomic resolution. We perform an atomically resolved mapping of the spatial orientation of the intercalated CH\textsubscript{3}NH\textsubscript{3}+ organic cations and the electrostatic potential at (001) cleavage surfaces in the as-cleaved state in dark and under laser illumination. We find an additional degree of freedom, a photodriven order transition of the organic cation dipole orientation pattern transforms a polarization structure with overlapping electron and hole transport paths in dark conditions into a new one under illumination with one-dimensional atomic-scale potential wells, creating separate conduction channels for electrons and holes. The underlying mechanism is suggested to be a photoexcited separation of electron–hole pairs in spatially displaced orbitals, creating a polarization field, which initiates a reordering of the intercalated polarized organic molecule cation. Analogous illumination-induced polarization order transitions in the bulk can be anticipated to be at the origin of the high efficiency and carrier conduction properties of organometal halide perovskites and their solar cells.

**RESULTS**

On the basis of the bulk structure of orthorhombic CH\textsubscript{3}NH\textsubscript{3}PbBr\textsubscript{3}, cleaved (001) surfaces can be terminated either by Pb–Br or by CH\textsubscript{3}NH\textsubscript{3}+–Br\textsuperscript{−} (MA-Br) layers (Figure 1A). In the corresponding constant-current STM images shown in Figure 1B,C, respectively, the bright protrusions reveal the positions of the Br surface atoms.\textsuperscript{17,29,31,32} The Pb–Br surface termination does not contain MA organic cations (see Figure 1A) and exhibits a \(2 \times 2\)-like rectangular pattern, resulting from the orthorhombic crystal structure. For the mapping of the dipole orientations of the intercalated MA organic molecule cations, the highest possible sensitivity is achieved at the surface termination with a MA-Br top layer. Figure 1C illustrates a typical cleavage surface with a MA-Br top layer, revealing two types of surface reconstructions labeled dimer and zigzag structure, highlighted in yellow and green, respectively.\textsuperscript{29,30} The dominant dimer structure exhibits alternatingly increased and reduced Br–Br separation along (110) directions, leading to dimers (Figure 1D). In contrast, the zigzag structure forms zigzag rows of Br atoms along the [100] direction (Figure 1E). The different surface reconstructions arise from different dipole orientation patterns of the intercalated MA (CH\textsubscript{3}NH\textsubscript{3}+) organic molecule cations.\textsuperscript{29} The Coulomb interaction between the negatively charged Br\textsuperscript{−} and the dipole of the polarized CH\textsubscript{3}NH\textsubscript{3}+ organic cation induces an attraction or repulsion depending on the orientation of the MA organic molecule cations. Hence, the displacements of the Br\textsuperscript{−} are the signatures of the orientation of the dipoles of the neighboring organic molecule cations, not visible themselves in the STM images.\textsuperscript{29} Figure 1D,E shows the dimer and zigzag structure with the dipole of the MA organic cations indicated by white arrows, respectively. For example, in Figure 1D, the two Br atoms nearby the positive side of the organic cations’ dipole are shifted toward the organic cation,
whereas those facing the negative side of the dipole are repelled, creating a $2 \times 2$ periodicity as indicated by the dotted unit cell.

To understand the effect of the dipole orientation of organic cations on the transport of free charge carriers, the local electrostatic potential landscape is deduced. The methodology is presented in the following first. A quantity directly related to the surface electrostatic potential $\Phi$ is the work function $\phi$ of CH$_3$NH$_3$PbBr$_3$, through $\kappa \Delta \Phi = \Delta \phi$. The spatial fluctuations of the work function of CH$_3$NH$_3$PbBr$_3$, $\Delta \Phi$, can be extracted from the exponential decay of the tunnel current ($I$) with tip–sample separation ($\Delta z$), given by

$$ I \propto \exp(-2\kappa \times \Delta z) \quad (1) $$

with $\kappa$ being the inverse decay constant

$$ \kappa = \frac{\sqrt{2mB}}{\hbar} \quad (2) $$

The energy barrier $B$ experienced by the tunneling electrons with mass $m$ is approximated by $B = (\Phi_{\text{Ti}} + \Phi)/2$, with $\Phi_{\text{Ti}}$ being the work function of the tungsten tip. Figures 2 illustrates such measurements: First, $I(\Delta z)$ curves measured on the dimer structure at the center position of a dimer (blue circle in Figure 2A) and between of dimers (red circle) are shown in Figure 2E. The solid lines illustrate a fit of eq 1 to the data revealing an exponential decay. The obtained $\kappa$ is mapped two-dimensionally in Figure 2B,D for surface areas with dimer and zigzag structure, respectively.

The $\kappa$ maps reveal characteristic spatial variations corresponding according to Eq 2 to fluctuations of the potential energy. Figure 2F shows the $\kappa$ values (left axis) measured at four equivalent positions between of two Br$^-$ atoms with different surrounding organic cation dipole alignments, as indicated by the respective arrows. For the dimer structure, the head-to-head and the tail-to-tail dipole alignments yield a $\kappa$ of $\sim 0.86$ and $\sim 0.81$ Å$^{-1}$, respectively, corresponding to an electrostatic potential energy difference of 0.68 eV. In contrast, in the zigzag structure with ferroelectric dipole alignments the potential energy difference between the Br$^-$ atoms is much smaller, that is, $\sim 0.12$ eV, consistent with theory

The derivation of the MA organic molecule cation dipole orientation pattern is corroborated by Figure 3A–C using the example of the dominating $2 \times 2$ dimer surface structure observed in dark. The calculated STM image (Figure 3B) based on the dipole pattern shown schematically in Figure 3C agrees excellently with the measured STM image (Figure 3A), corroborating ref 29.

Thus far, we only investigated the dipole orientation pattern in dark, without illumination. However, under laser illumination a fundamentally different new dominant $4 \times 2$ surface structure forms reversibly, characterized by a $\times 4$ modulation along the [110] direction and a $\times 2$ modulation along the perpendicular [110] direction (Figure 3D). The reversibility toward the $2 \times 2$ dimer structure in dark, shown in the Supporting Information (Figure S1), demonstrates the presence at all times of the organic cations. Hence, a photodriven reordering of the dipole orientations of the MA organic cations takes place.

Therefore, we derive a map of the surface organic cation dipole orientation by analyzing the displacements of the Br atoms observed at the surface along the three symmetry lines labeled A–A’, B–B’, and C–C’ in Figure 3D:

(i) The overall squarishlike structure and the observation of bright (high local density of states) and dark (low local density of states) stripes along the [110] direction indicates that the dipoles must be oriented primarily perpendicular to the surface plane but in the opposite direction, that is, the negative side up in the bright stripes (B–B’) and the positive side up in the dark stripes (C–C’).

(ii) The $\times 2$ periodicity along the [110] direction indicates that the dipoles in the center of the bright (B–B’) and dark (C–C’) stripes are in addition inclined along the [110] direction, resulting in a modulation of the degree of polarization and hence of the repulsive (attractive) forces exerted on the Br atoms in the bright (dark) stripes. This leads to the dipole orientation patterns along B–B’ and C–C’ illustrated schematically in Figure 3F.

(iii) Finally, taking into account the opposite perpendicular dipole orientation between the bright and dark stripes (see (i) above), the dipole of the organic cation between must be primarily in-plane oriented. Since the overall Br atoms exhibit an almost perfect square lattice, the in-plane dipoles of the organic cation are likely alternatingly pointing toward B–B’ and C–C’ lines. The resulting dipole orientation pattern along the A–A’ line consists of consecutive 90° rotated organic cations as schematically illustrated in the structural model in Figure 3F. The good agreement of the simulated (Figure 3E) and experimental STM images (Figure 3D) confirms the derived illumina-
The dipole orientation pattern under illumination is overall anti-ferroelectric. However, along the B−B′ and C−C′ lines the dipole orientations are always pointing down and upward, respectively, creating local ferroelectricity. This is corroborated by the nanoscale domain pattern observed in Figure 4. Two types of 4 × 2 domains occur alternatingly (labeled A and B domain), which are shifted against each other by half a unit cell along the ∥ direction. This leads to a nanoscale reversal of the out-of-plane organic molecule dipole orientations along the [110] direction, for example, along the B−B′ line. This formation of an anti-ferroelectrically ordered nanoscale domain pattern compensates the local ferroelectricity of the illumination induced 4 × 2 structure and corroborates the derived molecule orientation pattern.

The illumination also changes drastically the potential energy landscape. Figure 5A,D shows the spatial variation of the inverse decay constant \( \kappa \) extracted from \( I(\Delta z) \) curves measured at every pixel position without and with light illumination, respectively. A comparison of both inverse decay constant maps points to a very spotty distribution in dark, transforming to a one-dimensional pattern under illumination. To extract the potential energy landscapes \( e\Delta\phi \) local corrugation effects were removed by averaging the inverse decay constants within a 2×1 and 1×1 unit cell, respectively. The resulting potential energy landscapes without and with illumination are shown in Figures 5B,E, respectively. We also simulated the theoretical potential maps of the dimmer phase in the dark (Figure 5C) and the 4 × 2 structure under illumination (Figure 5F). Both simulated potential maps agree well with the experimentally observed ones.

In dark, the electrostatic potential energy landscape exhibits a weak checkerboard-like pattern over the entire cleaved surface with local minima and maxima (see Figure 5B). In contrast, under illumination (Figure 5E), the electrostatic potential energy landscape is dominated by a strong one-dimensional valley and hill pattern aligned along the [1−10] direction with significantly larger modulation as compared to the case without illumination.

**DISCUSSION**

This drastic modification of the potential energy landscape affects carrier transport: In the dark, the potential energy fluctuations are too weak to create spatially separate conduction channels for electrons and holes. In terms of transport paths, the spotty pattern of the potential energy fluctuations and the lack of orientational confinement create many crossing points of hole and electron pathways, as graphically suggested by the large fading out of the pathways (Figure 6A). Hence, the probability of recombination increases. However, under illumination the reordering of the organic cation dipoles creates deep one-dimensional potential energy wells with an average depth of \( \sim 150 \) meV. The one-dimensional potential wells can be rationalized on the basis of the relative orientation of neighboring organic cation dipoles. Along the atomic rows in [110] direction neighboring dipoles always exhibit a perpendicular arrangement (A−A′ in Figure 3F). As shown in Figure 4, formation-induced organic cation molecule dipole orientation pattern.
This 90° rotated arrangement leads to very small potential fluctuations. In contrast, in [110] direction, the organic cation dipoles have a head-to-head or tail-to-tail component (see model along B−B′ and C−C′ in Figure 3F), which was found to create a large potential energy modulation (Figure 2F). Hence, the light-induced organic cation dipole orientation pattern creates strong one-dimensional potential energy wells, avoiding crossing points of hole and electron pathways (Figure 6B), effectively increasing the carrier lifetime.

We found an atomic-scale dipole reordering upon illumination inducing fundamental transformations of the potential landscape at organometal halide perovskite cleavage surfaces. To check if the bulk material undergoes an illumination induced reordering too, we performed macroscopic resistance measurements of the same crystal. They yield a pronounced one-dimensional reduction in resistance upon illumination (Supporting Information 2), anticipating that illumination of organometal halide perovskites will induce reordering of the intercalated organic molecule dipoles in the bulk, too.

Finally, we turn to the physical mechanisms driving the photoinduced dipole reordering. The electromagnetic field of the incident light itself cannot account for the reordering, since a sub-bandgap illumination with same intensity does not induce any reordering. Similarly, following Fourier’s heat conduction law, the used laser irradiance induces only negligible heating (<2 K) for our sample dimensions and the materials’ thermal conductivity of 0.4−0.5 W m−1 K−1. Only when electron−hole pairs are photogenerated, a reordering takes place. This points to an electronically induced dipole reorientation via excited charge carriers, which can be explained as follows: Illumination induces a weakening of the Coulomb interaction between the halide atom and the MA molecule cations by photoexcitation of an electron from the hybridized Pb 6s−halide 5p orbital (at valence band maximum) into the Pb 6p orbital at the conduction band edge, as suggested by ref 20. This leads to a spatial separation of the electron and hole pair, due to the transfer of the electron from close to the halide atom site to the Pb site within the unit cell, creating a polarization field. One can anticipate that the intercalated polarized MA molecule cations rotates in this photoinduced polarization field to counteract it. It can be expected that the rotation is enabled by the prior...
weakening of the Coulomb interaction between the MA molecule cation and the halide atom and thus lowering of the rotation barrier by electron–hole pair generation. Hence, this suggests that the photonduced reordering of the MA molecule orientation pattern is a counteraction to a photonduced polarization arising from excitation in spatially shifted orbital states within a unit cell.

CONCLUSIONS

We discovered a photonduced atomic-scale reordering of the intercalated MA molecule cations at organometal halide perovskite surfaces using cross-sectional scanning tunneling microscopy. The rotation of the polarized MA molecule cations is suggested to be initiated by a photonduced polarization created by excitation of electron–hole pairs in spatially displaced orbital states. The reordering is connected with a fundamental transformation of the potential landscape toward one-dimensional potential wells, suggesting a separation of charge carriers and hence enhancement of carrier lifetimes. Macroscopic resistance data indicate that the photonduced reordering effect is also present in the bulk. This may in analogy lead to the creation of potential wells in the bulk, separating hole–electron pairs. The therewith expected increased carrier lifetime would provide an interpretation of the high photoelectric conversion efficiencies of organometal halide perovskites. Furthermore, our results indicate that MA molecule cation dipole (re)ordering by illumination needs to be generally considered as additional degree of freedom for understanding the perovskites’ characteristics and for reconciling of apparently contradictory properties. Such transitions are likely to be central for developing a comprehensive physical picture of charge carrier dynamics and high photovoltaic performance in organometal halide perovskites under actual operation conditions.

METHODS

Cross-Sectional STM Measurements. For our high-resolution STM imaging, we cleaved CH3NH3PbBr3 single crystals on their (001) plane in ultrahigh vacuum (∼2 × 10−11 mbar) at 4.3 K to expose a clean and stoichiometric cross section through the sample. CH3NH3PbBr3 (MAPbBr3) was chosen, because large single crystals, with high stability in air, can be grown easily, and the material exhibits a reproducibly cleavable (001) plane. Therefore, MAPbBr3 is used as a model system for the investigation of the light-induced dipole reordering with atomic resolution. Furthermore, in view of technological applications it is critical to investigate the orthorhombic phase of CH3NH3PbBr3. At room temperature, CH3NH3PbBr3 exhibits disordered orthorhombic distortions of the unit cells, whereas below 160 K a pure orthorhombic phase forms, exhibiting larger ordered domains with cell parameters of a = 7.97 Å, b = 8.58 Å, and c = 11.85 Å.42 In this work, we investigate the pure orthorhombic phase (T < 160 K) to unravel the fundamental molecular dipole ordering behavior in absence of grain boundaries and domain walls. This provides access to the intrinsic molecular dipole degree of freedom in organic–inorganic perovskites. The cleavage surfaces of the stable orthorhombic phase of CH3NH3PbBr3 were directly investigated with atomic resolution without interruption of the vacuum while keeping the samples cooled at 4.3 K. For measurements in the dark, the cooling shield was fully closed. For constant laser illumination we used a laser diode emitting unpolarized light of a wavelength of 532 nm focused onto the sample to reach a surface illumination of 500 eV, and the k-point meshes of (2 × 2 × 1) and (2 × 1 × 1) were used to sample the surface Brillouin zone for the dimer and 4 × 2 structures, respectively. To prevent an unphysical dipole interaction between two neighboring surfaces of a slab model and to obtain a correct local electrostatic potential, a dipole correction scheme39 was applied for all DFT calculations.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.8b09645.

The reversibility of the photodriven molecule reordering. We find again the same initial 2 × 2 dimer structure when illumination was turned off, which is directly induced by the presence of an anti-ferroelectric dipole ordering. The macroscopic resistance measurement of the MAPbBr3 crystal. We find that illumination leads to a drastic reduction of the resistivity along one direction only, while along the other direction the resistivity remains unchanged. This matches the illumination-induced change of the potential landscape observed in our STM measurements (PDF)

The light-induced reversible molecule dipole reordering is illustrated schematically (AVI)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was financially supported by the Ministry of Science and Technology of Taiwan (Contract No. MOST 106-2628-M-002-011-MY3), National Taiwan Univ. (Contract No. NTU-107L7848), and the Center of Atomic Initiative for New Materials, National Taiwan Univ., Taipei, Taiwan from the Featured Areas Research Center Program within the framework of the Higher Education Sprout Project by the Ministry of Education in Taiwan (108L9008). B.-C.H. acknowledges financial support from Academia Sinica through the investigator award (AS-IA-107-M03) given to Prof. Y.-L.W. The authors also
thank Prof. L.-M. Wang, T.-W. Yan, and T.-J. Khou for the macroscopic resistance measurement.

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