Distinct conducting layer edge states in two-dimensional (2D) halide perovskite

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Two-dimensional (2D) lead halide perovskite with a natural “multiple quantum well” (MQW) structure has shown great potential for optoelectronic applications. Continuing advancement requires a fundamental understanding of the charge and energy flow in these 2D heterolayers, particularly at the layer edges. Here, we report the distinct conducting feature at the layer edges between the insulating bulk terrace regions in the (C4H9NH3)2PbI4 2D perovskite single crystal. The edges of the 2D exhibit an extraordinarily large carrier density of ~10^{23} \text{cm}^{-3}. By using various mapping techniques, we found the layer edge electrons are not related to the surface charging effect; rather, they are associated with the local nontrivial energy states of the electronic structure at the edges. This observation of the metal-like conducting feature at the layer edge of the 2D perovskite provides a different dimension for enhancing the performance of the next-generation optoelectronics and developing innovative nanoelectronics.

INTRODUCTION

Two-dimensional (2D) halide perovskite heterostructures have created enormous excitement owing to their stronger photostability and chemical stability, photophysical tunability, photoabsorption, and emission characteristics. 2D halide perovskites exhibit remarkable electronic properties at room temperature that provide opportunities to advance applications from photodetectors to lasers, electro luminescence, and spintronics (1–4). Results on solar cells incorporating 2D halide perovskites have shown a decent power conversion efficiency of >15% (5) and a long-term stability of up to 1 year (6). Further efficiency boost while maintaining stability requires reduction of the large exciton binding energy and comprehensive understanding of the photophysical processes in the 2D halide perovskites.

The 2D halide perovskites, (RNH3)2(CH3NH3)_{n-1}MX3\geq n, are composed of a corner-sharing [MX6] metal halide network sandwiched between the organic barrier planes of RNH3. The variable n indicates the stacking number of the [MX6] network layers between two organic barrier layers. For the extreme case of n = 1, the thickness of the metal halide network decreases to the scale of de Broglie wavelength of the carriers, giving a strong quantum confinement effect on the charge behavior and representing a typical multiple quantum well (MQW) structure. It is prevailing agreed that in a halide perovskite MQW (pero-MQW), the spatial confinement confines the Bohr radius and quadruples the exciton binding energy in thin and deep QWs, (7), and the large discrepancy in dielectric constants between inorganic and organic layers even makes the exciton binding energy much larger (8). During a photovoltaic process, such a large binding energy will result in reduced charge dissociation into free carriers and thereby cause increased gaseous recombinative loss for the solar cells. The charge transport in pero-MQW is expected to be highly confined within the QW plane, as the electrons are freely movable within the in-plane direction but tightly confined in the out-of-plane direction, in analogy to the ideal 2D electron gas. However, at the edge of the pero-MQW or macroscopically at the interface or surface of the pero-MQW thin film in solar cells, understanding of the charge carrier behavior during transition from the 2D electron gas to 3D electrons, as well as the innate carrier recombination, interface scattering, and transport mechanisms at the boundary, remains challenge.

Various macroscopic techniques have been used to investigate the bulk properties of the pero-MQW film. In principle, a 2D pero-MQW is expected to provide 100% luminescence quantum yield as it has natural out-of-plane self-termination without any dangling bonds. However, the pero-MQW bulk crystal experimentally exhibits low quantum yields (9–11), indicating an unclear missing part linking to the quantum loss. The near-perfect vertical oriented bulk pero-MQW film with larger QW thickness [(C4H9NH3)2(CH3NH3)_{n-1}PbI3\geq 3, n = 3 and n = 4] has been reported to exhibit an in-plane charge carrier mobility (12) comparable to that of CH3NH3PbI3 (13). While contactless time-resolved microwave conductivity measurements contradictorily suggest a much lower carrier lifetime of the same material (13). Recent investigations in the quasi-2D perovskite suggested a scaling law for excitons (14, 15), and solar cells based on 2D/3D mixed halide perovskites have shown the success for simultaneously improved power conversion efficiency and stability (12, 16–18), which, however, raises the fundamental questions about the depleted and accumulated charge carriers at the 2D/3D hetero-interfaces, similar to the issues in GaAs/AlxGa1-xAs superlattice (19), since the 3D perovskite has an energetically lower conduction band and may act like an electron acceptor in the 2D/3D mixed phase. Overall, these contradictory results from different reports and the questions about the nontrivial boundary relevant properties cannot be completely explained by solely considering the bulk physics without taking into account the edge effect. Investigating the nature and functionality of the layer edge states (ES) is the motivation behind this study.

The ES in conventional inorganic MQWs have extraordinary properties. For example, in HgTe QWs, the nontrivial ES enable the dissipationless 1D electrical conduction that is immune to scattering from nonmagnetic impurities (20). In addition, in particular MQW systems, the existence of Majorana fermions enables the superconductivity in the quantum spin Hall edge (21). For the pero-MQWs, Blancon et al. reported the free carriers at layer edges of quasi-2D pero-MQWs [(C4H9NH3)2(CH3NH3)_{n-1}PbI3\geq 3] that can sufficiently accelerate the exciton dissociation for photovoltaic conversion (22). However, for 2D pero-MQWs, there is lack of fundamental investigations on the layer ES, particularly the electrical feature. Here, we report the direct observations of the distinct conductive layer ES in the 2D...
pero-MQW single crystal, namely, \((\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbI}_4\) \((n = 1)\), using conducting atomic force microscopy (c-AFM), scanning electron microscopy (SEM) mounted with secondary electron and back-scattered electron detectors, and confocal Raman and photoluminescence (PL) mapping techniques. The c-AFM is a widely used technique to visualize the nanoscopic landscape as well as the corresponding electronic characteristics. We found an extraordinary conducting feature along the topographical ES contour in the 2D pero-MQWs, while the bulk terrace region remained insulated. The ES are occupied by free carriers in lower energy levels compared to those of bulk 2D pero-MQWs, and the calculated free carrier density in the ES region exhibits a large value on an order of \(10^{21}\) cm\(^{-3}\), which is close to that in metals \((\sim 10^{22}\) cm\(^{-3}\)) and invariant with respect to the edge height, scanning conditions (i.e., the scanning directions, scanning speed, and scanning times), illumination intensities, or sample bias. This discovery of the ES in 2D halide pero-MQWs provides a new operational methodology for enhancing charge transport in optoelectronic applications and innovative opportunities for 1D electrical conduction in nanoelectronics.

RESULTS

Direct observations of the layer edge current between adjacent insulating terraces

To investigate the fresh ES in the \((\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbI}_4\) pero-MQWs, we synthesized the single-crystal thin film from the water-air interface according to our previously reported methods \((23)\) and exfoliated several top layers before the c-AFM measurement. Figure 1A schematically describes the \((\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbI}_4\) pero-MQWs structure, where the QW thickness of 6.3 Å, the barrier thickness of 7.6 Å, and crystal orientations are calculated from the x-ray diffraction (XRD) data (fig. S1A). Figure 1B presents the c-AFM setup for detecting the out-of-plane current and the topographical information of the pero-MQWs. The sample is placed on a silver substrate and in contact with the top platinum-coated tip. After scanning at 2 Hz at room temperature in the dark, we found an insulating feature in the bulk terrace region but an unexpected current along the contour of the layer edges. As shown in the topographical map (Fig. 1C), the pero-MQWs exhibit a terrace feature with atomically flat large QW planes parallel to the substrates and sharp layer edges along the out-of-plane \((z\)-axis\) direction. The edge height difference \((\Delta z)\) ranges from nanometer to micrometer depending on the number of the QW layers. From the current map (Fig. 1D), the current in the bulk terrace region is negligible regardless of the altitude, but at the sharp layer edges, there exists a continuous current. The larger the edge height difference, the higher is the detected current. Figure 1E shows the \(z\)-profile along a longitudinal line in the \(x\)-axis direction, as marked in fig. S1 (C and D). By taking the first derivative of \(z\)-profile and comparing it with the corresponding current profile, we found that there is a notable consistency (Fig. 1F) in terms of the peak position. Such an observation verifies that the detected current only exists at the sharp layer edges and is notably related to the edge height difference as it links to the area under peaks (i.e., the integration of the \(z\)-profile derivation). On the other hand, the current in the bulk terrace region remains zero, suggesting an insulating characteristic.

Fig. 1. Direct observations of the layer edge current between adjacent insulating terraces. (A) Schematic of the 2D \((\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbI}_4\) pero-MQW structure with a QW layer thickness of 6.3 Å and a barrier layer thickness of 7.6 Å. (B) Schematic layout for c-AFM measurement in contact mode, where the QW plane is parallel to the metal substrate. (C and D) 3D image of (C) topographical and (D) current map of the 2D pero-MQW sample. (E and F) Corresponding (E) height profile \((z\)-profile\) and (F) comparison of first derivative of \(z\)-profile and current profile, along a longitudinal line in the \(x\)-axis direction (designated in fig. S1, C and D).

can be ascribed to the insulating organic layers that are periodically inserted within the MQWs, and the out-of-plane conductance is negligible (discussed later). The conducting sharp layer edges in the pero-MQW are related to the free charge carriers residing at the layer ES.

Layer ES along the contour direction

The continuous current detection along the edge contour direction suggests an edge height difference–related carrier number. To investigate the current dependence on the edge height difference, we consider the local small region along the contour direction as an analytical unit. Figure 2 (A and B) shows the starting positions and the analytical unit marked in red and green in the topographical and current map, respectively. Figure 2C exhibits the 3D model of the corresponding local analytical unit, where we further extract a wedge for current normalization from an effective charge injection region (ECIR) that is exclusively responsible for the charge injection during the contact. Briefly, when the c-AFM probe interacts with the layer edge region of the pero-MQWs, charge carriers (either electrons or holes) are injected from the pero-MQWs to the probe. The contact area can be determined by the nanoindentation (8) from the contact geometry, which could be estimated through the Hertz method, according to the equation of

\[ F = \frac{4}{3} \frac{E}{1 - \nu^2} \sqrt{R \delta^3} \]  

where \( F \) is the force applied by the tip, \( E \) is the Young’s modulus, \( \nu \) is the Poisson’s ratio of the sample, and \( R \) is the radius of tip curvature. While beyond the intimate contact region, charge carriers from the deeper region inside the perovskite may also contribute to the injection. In parallel, the contact between the metal probe and the perovskite semiconductor will evoke a depleted region in the perovskite, within which the mobile carriers are depleted and contributed to the current detection by the c-AFM. Hence, the spatial extension of the depleted region defines the volume of the ECIR. During the scan across the layer edge, total collected charges are exclusively contributed by the whole ECIR volume at the layer edge, which can be estimated on the basis of the contact geometry determined by the Hertz method and current-driving voltage derivation from Poisson’s equation and Ohm’s law in spherical coordination (details are provided in note S1). Consequently, a schematic of the resultant truncated cone-shaped individual ECIR was shown in the wedged edge region of the analytical unit (Fig. 2C). To study the current development along the contour direction, we assigned evenly distributed 26 analytical units along the contour direction (dashed arrow in Fig. 2A), each having a 1-μm width in the \( y \) direction for noise elimination and a 4-μm length for covering the whole layer edge region in the \( x \) direction. The corresponding current profile of the first analytical unit at the starting position is shown in Fig. 2D with the corresponding \( z \)-profile and the current integration with respect to the in-plane distance \( x \) across its layer edge. The \( z \)-profile is well matched with the current integration. These observations also apply to the other 25 analytical units at different contour positions along the dashed arrow (fig. S2). The summarized \( z \)-height difference (\( \Delta z \)), peak current values, and current integration across the layer edges at different contour positions are further compared in Fig. 2E. In contrast to the peak current, the current spatial integration across the layer edges (i.e., along the in-plane \( x \) direction) is better matched with the \( z \)-height difference in terms of different contour positions, suggesting an underlying relationship between \( \Delta z \) and current spatial integration. \( \Delta z \) corresponds to the whole volume of ECIR, while the current spatial integration is related to the total collected mobile charges and the scan rate in the experiment, as derived by the following equation

\[ \int I \cdot dy = \int \frac{dQ}{dt} \cdot dy = \int u \cdot dQ = u \cdot \int dQ \]  

where \( I \) is the detected current, \( dQ \) is the differential of charges of free carriers, \( t \) is time, and \( u \) is the local scan rate along the \( x \) direction in the analytical unit, which can be determined by navigating the wedge’s orientation in the \( X-Y \) coordinate system of the panorama current image (taking the first analytical unit as an example, the speed along the unit’s \( x \) direction is \( u = u_{X-Y} = u_{X-Y} \cdot \cos \theta \), where \( u_{X-Y} \) is the scan rate in the \( X-Y \) coordinate system of the panorama current image, i.e., the experimental scan rate, and \( \theta \) is the angle between the cartesian coordinate systems of the analytical unit and the panorama current image, as schematized in fig. S2B). Thus, the total
collected mobile charges across the layer edges can be calculated. Figure S3A exhibits the total collected charges and the ECIR volume of each analytical unit at different topographical contour positions. The linear relationship suggests a constant charge carrier density at the layer edge (fig. S3B), regardless of different contour positions. The free charge carrier density was further calculated in terms of different contour positions. As shown in Fig. 2F, the carrier density keeps invariant in regard to different positions along the edge contour direction, where the peak current and edge height can be different (Fig. 2E). The carrier density at the ES is calculated to be \(1.1 \times 10^{21} \text{ cm}^{-3}\) (close to that of metals, \(-10^{22} \text{ cm}^{-3}\)), which is significantly larger than that in typical inorganic semiconductors such as germanium (\(1.83 \times 10^{13} \text{ cm}^{-3}\)), silicon (\(8.81 \times 10^{9} \text{ cm}^{-3}\)), or gallium arsenide (\(2.03 \times 10^{6} \text{ cm}^{-3}\)) (24), around 10 orders of magnitude larger than that in bulk perovskite crystals in the dark (25, 26) and six orders of magnitude larger than that in sufficiently illuminated bulk perovskite (27). Fundamentally, the density of electrons in a semiconductor is related to the density of occupied states that is simply the product of the density of states (DOS), and the Fermi-Dirac probability function for DOS occupation. The DOS responsible for conduction are the states at the bottom of the conduction band, as the minimal point of the dispersion curve \(E(k)\) in momentum space for the electron has a parabolic behavior with a modified effective mass, which can be analogous to the free electron in vacuum moving in a periodic potential (28). The conducting nature at the layer edges is therefore related to electronic states near the conduction bottom, which are supposed to be substantially different from those in the bulk crystals.

**Scan rate effects on layer edge currents**

We have shown in Eq. 2 that the total detected charges depend on the measured current and the scan rate. To verify the interrelationship between these two parameters, the current map under different scan rates is investigated in Fig. 3A. An increase in current with the scan rate is observed. Figure 3 (B and C) exhibits the average \(z\)-profile and current profile along the arrow direction in the analytical unit (fig. S4A), respectively, under different scan rates. The terrace region exhibits a constant zero current regardless of the scan rates, while the layer edge exhibits a monotonous increase in current as the scan rate increases. Figure S4B displays a linear relationship between the peak current at the layer edge and the scan rates. In addition, as shown in Fig. 3D, at the terrace positions (positions B and C), the current integration increases linearly with the scan rate, while at terrace positions (position A), as the current shows no response, the current integration remains zero. We further calculated the charge carrier density at both layer edge positions from the total charges obtained by the current integration over the scan rate with a cosine correction and the whole ECIR volume. The charge density at different edge positions exhibits the same order of magnitude of \(-10^{21} \text{ cm}^{-3}\), regardless of various scan rates (Fig. 3E). This value agrees well with those obtained from different samples at varying contour positions (Fig. 2F).

**Layer edge current direction study by tuning scan directions and sample bias**

In contrast to the insulating terrace region where the current is constantly zero, there is either a positive or negative detected current at the layer edge regions. To investigate the current direction dependence on the sample topography and the scan direction, we measured both the trace (from left to right) and retrace (from right to left) currents on various 2D halide pero-MQW samples with different layer edge heights. As shown in Fig. 4A and fig. S5 (A and B), when the probe ascends the layer edges (position C in trace scanning and position A in retrace scanning in Fig. 4B), the current shows a negative feature (electron flowing from the sample to the probe); when the probe descends the layer edges (position A in trace scanning and position C in retrace scanning in Fig. 4B), the current displays a positive feature (electron flowing from the probe to the sample). Consequently, an uphill movement of the probe at the layer edge will contribute a negative current, whereas a downhill movement will render a positive current, regardless of the sample orientation or the scanning direction. The possible mechanism on the conversion of the current polarity at the layer edge depending on the probe dynamics might be related to the dynamics of the ES charge consumption and refilling assumption (details are specified in note S2). A comprehensive understanding may require future in-depth experimental elucidations and proper modeling tools in the future. Here, we also tracked the trace and retrace current under different sample biases (fig. S5, C and D) while keeping the tip being grounded. The calculated carrier density at positions A and C exhibits the identical number of \(1.1 \times 10^{21} \text{ cm}^{-3}\), regardless of the scanning direction. It should also be noted that at different sample biases ranging from \(-8\) to \(8 \text{ V}\), there is no large change in carrier density of layer ES, owing to the unchanged current profile (fig. S5, F and G). This is due to the bulk insulating feature of the 2D halide pero-MQWs in the out-of-plane direction, which makes the sample surface hardly affected by the sample bias applied at the sample bottom (detailed in note S3).

**Illumination influence on the layer edge current**

When exposed to light, photogenerated electron-hole pairs appear in the bulk of the 2D pero-MQWs, and the further dissociation into free carriers leads to the photovoltaic effect in solar cells. To investigate whether the illumination will affect the ES in the 2D pero-MQWs, we performed the c-AFM measurement under dark conditions and under different light intensities. As shown in Fig. 5A, by tuning the illumination intensity, the current landscape shows no obvious changes. To quantify the current profile across the layer edges, an analytical unit is constructed (marked in Fig. 5A), and the average \(z\)-profile and current profile along the specified in-plane direction are compared in terms of different light intensities, in Fig. 5 (B and C, respectively). The \(z\)-profile is not affected by the illumination as expected. The current did not show noticeable changes upon the illumination either (Fig. 5C). We further compared the current dependence on the illumination intensity at both layer edges and terrace positions. As shown in Fig. 5D, layer edges (positions A and B) exhibit the constant currents, and the terrace (position C) region shows zero current, regardless of the illumination intensities. The zero-current detection at the terrace region (position C) might be ascribed to the insulating feature of 2D pero-MQW in the out-of-plane direction, the large exciton binding energy that limits the free carrier density and the large injection barrier between the sample and tip. In the case of layer edge (positions A and B) regions, there is no photocurrent gain as the illumination intensity increases. As shown in Fig. 5E, under illumination intensities ranging from 5 to 40 mW/cm², the carrier density keeps invariant about \(1.4 \times 10^{13} \text{ cm}^{-3}\), which is identical to that in the dark (\(1.3 \times 10^{13} \text{ cm}^{-3}\)), indicating no additional photogenerated carriers contributing to the layer ES. The observation of the nonillumination-related ES current in the layer edges of 2D pero-MQW differs greatly from that in the bulk of typical semiconductors having a photocurrent gain under higher light intensities.
**DISCUSSION**

**Insulating feature in bulk terrace region**

The terrace region of the 2D pero-MQWs exhibits the insulating feature, regardless of the c-AFM scan speed, scan direction, light bias, or sample bias, which suggests a negligible out-of-plane (or perpendicular) carrier transport. The organic barrier layer has a much wider bandgap than the well layer, and hence, the induced large energy barrier makes the typical band transport impossible (29). Alternatively, perpendicular transport in traditional heterostructure MQWs [e.g., GaAs/AlAs (30), GaAs/AlGaAs (31), and InGaAs/InP (32)] has been studied with various carrier dynamics including carrier scattering, thermalization, escape, and capture (33–37). In particular, two transport processes have attracted considerable interest: the thermionic transport that postulates the energetic carriers with an energy equal to or larger than the top of the barrier will cross the barrier, and the quantum-mechanical tunneling through the barrier that takes into account the wave nature of the carriers, allowing them to penetrate through thin barriers. In the case of the terrace region of 2D pero-MQWs, electrons and holes are heavily bonded with a large binding energy of ca. 470 meV (discussed in note S4), significantly larger than the thermal energy at room temperature. Even if free charges are introduced into the 2D pero-MQWs through either photogeneration or injection from an electrode, they are most likely to form the exciton or further be recombined, instead of the formation of energetic free carriers. Meanwhile, the injection barrier also needs to be taken into consideration. In parallel, the tunneling probability through a QW structure can be calculated using the Wentzel–Kramers–Brillouin (WKb) approximation (38) from a simplified model and the probability of tunneling through a single barrier layer can be written as

\[ P_t(E) \approx e^{-\frac{md^2}{\hbar^2}} \]  

**Fig. 3. Scan rate effects on the layer edge current.** (A) Topographical and current images under different scan rates. (B) Average z-profile and (C) the corresponding average current profile extracted from the analytical unit, along the arrow direction in (A), under different scan rates. (D and E) Dependence of the (D) current integration and (E) charge carrier density on the scan rate at layer edge positions (i.e., positions B and C), and at the terrace region (position A).
where $\Delta E$ is the barrier height and $m$ and $\hbar$ are the free electron mass and Planck’s constant. Assuming a rational 6-eV bandgap of the barrier layer (39), the probability of the free carriers tunneling through a single organic barrier in $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbI}_4$ is calculated to be $2 \times 10^{-7}$.

Taking account of the periodic MQW structures, the out-of-plane quantum-mechanical tunneling through the multiple barrier layers will be negligibly small. As a result, the terrace region in the $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbI}_4$ pero-MQWs exhibits a constantly zero current as observed in our c-AFM measurement.

Conducting feature at the layer ES

In notable contrast to the bulk terrace region, the detected robust current with an extraordinarily high carrier density of $\sim 10^{21} \text{ cm}^{-3}$ at the layer edges suggests the presence of extraordinary ES. Since these free carriers reside at the sharp layer edges, one may argue that they can be caused by the charging effect. However, after 20 times of scanning of the c-AFM measurement, we found that there is no noticeable variation in the current intensity at the same layer edge position (fig. S6). This highly repeatable current suggests that the electrons more likely originate from the intrinsic ES of the material itself rather than the accumulation of space static electric charges that could be consumed after several scan times. We further used scanning electron microscope measurements mounted with secondary electron and backscattered electron detectors to distinguish the layer ES electrons from those in the bulk terrace region (detailed in note S5). The layer edges exhibit distinctly higher secondary electron intensity in comparison to the bleak bulk terrace region (fig. S7B), owing to the large density of free ES electrons that could elastically collide with the incoming electrons and produce the secondary electrons that can easily escape and get collected by the detector. Meanwhile, there are no charging effect–induced artifacts, image deformation, distortion, or shift found in the SEM images. Overall, these free ES electrons are essentially related to the intrinsic electronic structure at the layer edges of the 2D pero-MQWs, which are expected to be distinctly different from those in their bulk terrace region.

To correlate the detected free carriers at the ES with the energy states and quantify the energy information, we used a confocal spatial PL mapping technique to investigate the PL landscape in both bulk terrace region and layer edges. Because the $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbI}_4$ ($n = 1$) sample has a larger bulk bandgap than the limit of the incident photon energy ($\sim 2$ eV) of the equipment, we used the narrower-bandgap pero-MWQ single crystals of $(\text{C}_4\text{H}_9\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_2\text{Pb}_3\text{I}_{10}$ ($n = 3$) and $(\text{C}_4\text{H}_9\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_3\text{Pb}_4\text{I}_{13}$ ($n = 4$) to measure the PL landscape. Figure S8A shows the optical macroscopic images of the $(\text{C}_4\text{H}_9\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_3\text{Pb}_4\text{I}_{13}$ ($n = 4$) pero-MWQs, with a designated square region for PL mapping. Figure 6 (A and B) exhibits the PL landscape probed at 1.89 and 1.66 eV, respectively. The 1.89 eV corresponds to the bulk optical bandgap of the crystal, and we found that the terrace region shows strong PL intensity at 1.89 eV compared with the layer edges. When probed at 1.66 eV, the bulk terrace region hardly exhibited any PL signal, but the layer edges show a strong one. To quantify the PL with the photon energy in different topographical regions, we monitored the PL spectra at three different positions. As shown in Fig. 6C, only one peak corresponding to the bulk optical bandgap has been observed in the terrace regions (positions A and C), whereas for the layer edge position (position B), besides the bulk PL peak, there is an additional PL signal peaked at 1.66 eV. We also measured the PL landscape of the $(\text{C}_4\text{H}_9\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_2\text{Pb}_3\text{I}_{10}$ sample.
(n = 3) pero-MQW sample. The corresponding optical microscopic image (Fig. S8B) was recorded along with the PL landscape mapped at 1.95 eV (Fig. 6D) and 1.66 eV (Fig. 6E). Here, we used the 1.95 eV as the threshold value because a higher probe energy value will interfere with the incident photons. By checking different topographical positions, we found that the bulk terrace regions (positions A and C) still exhibited the PL peak identical to that of bulk crystals, while the layer edge position (position B) showed an additional PL peak at 1.66 eV (Fig. 6F). Hence, in comparing both pero-MQW samples, in spite of the change in the QW thickness (n = 3 and n = 4), there exist lower energetic states (1.66 eV) at the layer edges, which are responsible for the radiant recombination at longer wavelengths. It is reasonable to extrapolate that, in the (C_6H_{15}NH_3)_2PbI_4 (n = 1) pero-MQWs, there are also lower energetic states at the layer edges where the free carriers can reside. Figure 6 (G and H) schematically describes the MQW structure and the corresponding energy level diagram of the pero-MQWs, respectively. In the bulk terrace region, the charges are confined within the QW plane, where the periodically inserted insulating barrier layers make the out-of-plane charge transport impossible. Even under illumination, the strong quantum and dielectric confinement make the photoexcited states exist in the form of excitons instead of free energetic carriers. This, combined with the low tunneling probability, leads to the zero-current detection by the c-AFM at the terrace region, while at the layer edges, there are nontrivial energetic states (referred to as layer ES) that electrons can occupy. These ES electrons are then responsible for the current detection by the c-AFM measurement. From the PL measurement, these lower energetic ES are responsible for the PL response at 1.66 eV, and such an additional longer wavelength peak
suggests a smaller optical bandgap at the layer edges when compared with bulk terrace regions.

In summary, we found the nontrivial conducting phenomena at the layer edges in contrast to the insulating terrace region in the (C₄H₉NH₃)₂PbI₄ 2D pero-MQWs by performing microscopic mapping techniques including c-AFM, SEM, confocal Raman, and PL measurements. An extraordinarily high free carrier density of \( \sim 10^{21} \text{ cm}^{-3} \) has been estimated at the layer edges. SEM, confocal Raman, and PL measurement suggest that these free carriers are not correlated with the exotic chemical components or surface charge accumulation; rather, they originate from the nontrivial energetic ES at layer edges. These ES are distinguished by their phenomenal conductive nature as compared to the insulating feature of the bulk terrace region. Our observations on the distinct conducting nature at layer edges of the 2D pero-MQW opens a different dimension for the investigation of ES on the performance of perovskite optoelectronics and offers great opportunities for designing novel nanoelectronics.

**MATERIALS AND METHODS**

**2D pero-MQW sample preparation**

The single-crystal samples of \((\text{C}_4\text{H}_9\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_{n-1}\text{Pb}_n\text{I}_{3n+1}\) pero-MQWs \((n = 1, 3, \text{ and } 4)\) were synthesized according to the previously established methods (23). Briefly, lead(II) oxide \((1.126 \text{ g}, 2.4 \text{ mmol})\) was dissolved in hydroiodic acid \((5 \text{ ml})\) with hypophosphorus acid solution \((850 \text{ ml})\) and stirred at 100°C until a pale yellow solution was obtained. Methylammonium iodide and \(n\)-butylamine in different molar ratios \((n = 1, \text{ C}_4\text{H}_9\text{NH}_3\text{I} = 5 \text{ mmol}; n = 3, \text{ C}_4\text{H}_9\text{NH}_3\text{I} = 1.7 \text{ mmol and CH}_3\text{NH}_3\text{I} = 1.7 \text{ mmol}; n = 4, \text{ C}_4\text{H}_9\text{NH}_3\text{I} = 1.2 \text{ mmol and CH}_3\text{NH}_3\text{I} = 1.9 \text{ mmol})\) were slowly added into another vial containing \(3 \text{ ml} \) hydroiodic acid with an ice-water bath. After achieving a transparent solution, the ammonium precursor solution was carefully added into the lead solution for obtaining a transparent yellow solution at higher temperature. The hot solution was then cooled at a very slow rate of \(1^\circ\text{C}/2 \text{ hours}\). A single-crystal thin film grew within minutes at the water-air surface. The obtained

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**Fig. 6. PL study showing the lower energetic states at the layer edges.** Confocal PL mapping measurements on \((\text{C}_4\text{H}_9\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_{n-1}\text{Pb}_n\text{I}_{3n+1}\) pero-MQWs: the PL landscape probed at (A) 1.89 eV and (B) 1.66 eV, and the (C) PL spectra of different topographical positions. Confocal PL mapping measurements on \((\text{C}_4\text{H}_9\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_{n-1}\text{Pb}_n\text{I}_{3n+1}\) pero-MQWs: the PL landscape probed at (D) 1.95 eV and (E) 1.66 eV, and the (F) PL spectra of different topographical positions. Proposed layer ES mechanism: (G) schematics of MQW structure and (H) correlated electronic band structure. The electron-hole pairs in the bulk terrace region are tightly bonded, while at the layer edges, additional ES electrons reside, which are responsible for the detected current by the c-AFM measurement. The ES PL peak at 1.66 eV in \(n = 3\) and 4 samples suggests that the ES has a lower optical bandgap than that in the bulk terrace region. \(E_g\), energy bandgap. a.u., arbitrary units.
crystals were then moved to a vacuum oven with 40°C overnight storage for future use.

c-AFM measurement

The flat crystal was connected to the silver substrate by silver paste, with the QW layers parallel to the substrate. The crystal orientation was verified by XRD patterns obtained from Philips Xpert Pro X-ray Síffractometer (Almelo, The Netherlands) using Cu-Kα radiation (fig. S1A). The c-AFM measurement was performed using the Park XE7 system in the contact mode with a Pt-coated tip. To eliminate the concerns on surface contamination by the solution environment on samples, we exfoliated the samples to obtain a fresh top surface for the c-AFM measurement. The whole setup was installed in a mating chamber from Park Systems Corp to minimize the ambient disturbance. The experiment was carried out at room temperature with the gas environment of ambient air (78 volume % nitrogen and 21 volume % oxygen) with a relative humidity of ~30% at 1 atm. During the measurement, a Ag/pero-MQW/ Pt diode was constructed. The silver substrate acts as the bottom electrode and the top-conducting tip on a cantilever serves as the mobile top electrode reflecting both the electrically conductive feature and surface topographical character of the sample (optical lever method). The sample was applied on the bottom silver electrode with the top tip electrode grounded. Note that the energy difference between the Fermi levels of the sample and the work function of the Pt electrode should be taken into consideration for this microscopic mapping. The light bias was provided by an MK-R 12-V light-emitting diode (CREE, Durham, NC). The illumination intensity was tuned through a computer-controlled program from 0 to 70 mW/cm², as calibrated separately by a standard silicon solar cell. A ~5-mW infrared (860 nm) beam was used to reflect the tip deflection by the AFM, which was expected to cause negligible influence on the measurement as the absorption edge of the 2D pero-MQWs was far below 860 nm, and the shadow of the overhanging cantilever on the interrogated region could also significantly dilute the infrared photons.

SEM measurement

SEM images were obtained from Quanta 600 FEG, FEI, which was equipped with both a secondary electron detector and a backscattered electron detector (InLens). The sample was attached onto a conducting substrate by conducting paste. The sample surface was exposed without any metal coating during the measurement.

Confocal Raman and PL microscopic mapping measurement

Confocal Raman microscopic mapping measurement was performed on a WITec alpha500 equipped with a confocal Raman microscope for 3D chemical imaging. The sample was prepared on a quartz substrate. A laser beam with a wavelength of 633 nm was used as the incident beam in contact with an optical fiber. For the (C₄H₉NH₃)₂PbI₄ (n = 1) 2D pero-MQW sample, such incident photon energy is smaller than the bandgap, only causing the vibrational and rotational Raman shift. For (C₄H₉NH₃)₂(CH₃NH₃)₂PbI₁₀ (n = 3) and (C₄H₉NH₃)₂(CH₃NH₃)₃PbI₁₃ (n = 4) samples whose absorption edge is higher, strong PL signals were collected by the detector. Thus, for different samples, separate Raman and PL information were visualized along with the landscape.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/5/7/eaau3241/DC1

Fig. S1. 2D pero-MQW structural and optical properties and direction observations of the layer edge current.

Fig. S2. Layer edge current development along the contour direction.

Fig. S3. Layer edge charge distribution along the contour direction.

Fig. S4. Scan rate effects on layer edge current.

Fig. S5. Layer edge current polarity study.

Fig. S6. Repeatability of the layer edge current.

Fig. S7. SEM and confocal Raman mapping study of layer ES.

Fig. S8. Optical image of pero-MQWs.

Fig. S9. Hertz method analysis on the tip contact with samples.

Fig. S10. Possible mechanisms for the current polarity conversion at the layer edges.

Note S1. Estimation of ECR and charge carrier density.

Note S2. Conjecture of the current polarity conversion at the layer edges.

Note S3. Sample bias influence on layer edge currents.

Note S4. Large exciton binding energy in 2D pero-MQWs.

Note S5. Surface charge effect exclusion study by SEM and confocal Raman mapping measurements.

Appendix S1. The c-AFM edge current on samples of (C₄H₉NH₃)₂(CH₃NH₃)₃PbI₁₅ (n = 2, 3, 4, and ∞).


Acknowledgments: We extend acknowledgment to W. Leng from ICTAS for the help in confocal Raman and PL mapping measurement. Funding: This work was supported by Air Force Office of Scientific Research (FA9550-17-1-0341), Army SBIR program (Nanosonic), and Office of Naval Research (N000141712520). Author contributions: Kai Wang, C.W., D.Y., and S.P. conceived and designed the experiments. Kai Wang carried out the sample preparation, Kai Wang, Ke Wang, and Y.J. performed the microscopic characterizations and data analysis. All authors contributed to the results, discussion, and revision of the manuscript. Competing interests: The authors declare that they have no competing interests. Data and materials availability: All data needed to evaluate the conclusions are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

Submitted 29 May 2018
Accepted 6 June 2019
Published 12 July 2019
10.1126/sciadv.aau3241

Distinct conducting layer edge states in two-dimensional (2D) halide perovskite

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Sci Adv 5 (7), eaau3241.
DOI: 10.1126/sciadv.aau3241

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