

Deterministic Synthesis of a Two-Dimensional MAPbI₃ Nanosheet and Twisted Structure with Moiré Superlattice

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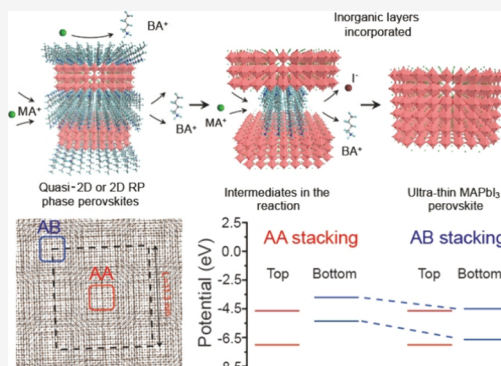


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ABSTRACT: The synthesis of extremely thin 2D halide perovskites and the exploration of their interlayer interactions have garnered significant attention in current research. A recent advancement we have made involves the development of a successful technique for generating ultrathin MAPbI₃ nanosheets with controlled thickness and an exposed intrinsic surface. This innovative method relies on utilizing the Ruddlesden–Popper (RP) phase perovskite (BA₂MA_{n−1}PbI_{3n+1}) as a template. However, the precise reaction mechanism remains incompletely understood. In this work, we systematically examined the dynamic evolution of the phase conversion process, with a specific focus on the influence of inorganic slab (composed of [PbI₆]^{4−} octahedrons) numbers on regulating the thickness and quality of the resulting MAPbI₃ nanosheets. Additionally, the atomic structure is directly visualized using the transmission electron microscopy (TEM) method, confirming its exceptional quality. To illustrate interfacial interactions in ultrathin structures, artificial moiré superlattices are constructed through a physical transfer approach, revealing multiple localized high-symmetry stacks within a distinctive square moiré pattern. These findings establish a novel framework for investigating the physics of interfacial interactions in ionic semiconducting crystals.



1. INTRODUCTION

Organic–inorganic hybrid halide perovskites with a typical three-dimensional (3D) framework stand out in photovoltaic research due to their remarkable electrical and optical properties,^{1–4} including high carrier mobilities, long carrier diffusion lengths, high absorption coefficients, and tunable optical bandgaps.^{5–8} Unlike conventional III–V semiconducting materials, one of the most attractive features of perovskites is their easy bandgap engineering, which can be achieved by controlling stoichiometry and/or dimensionality.^{9,10} The strong correlation between structures and optical properties enables the rapid development of preparation methods and synthetic conditions for exploring various dimensionalities of perovskites.^{11–13}

In recent years, significant advancements have been made in the development of low-dimensional (LD) lead halide perovskites, ranging from zero-dimensional quantum dots and nanoparticles^{14,15} to one-dimensional nanowires and nanorods,^{16,17} and two-dimensional nanosheets and nanoplates.^{18,19} The distinct characteristics resulting from reduced dimensions, such as quantum confinement effects, high photoluminescence quantum yield, and tunable band structures, hold substantial potential for fundamental research in physics and their incorporation into contemporary high-performance light-emitting devices.^{20,21} Notably, the attention

has been drawn toward layered two-dimensional (2D) perovskites, composed of nanometer-thick layers of hybrid halide perovskite separated by organic cation-based spacing layers, due to their improved stability and structural adjustability.^{22,23} Among all kinds of 2D perovskites, a prominent example is the Ruddlesden–Popper (RP) perovskites with the chemical formula L₂A_{n−1}B_nX_{3n+1}, where L represents monovalent bulky ligands with alkyl or aromatic components, A denotes a small organic cation, B signifies a metal cation, X stands for a halide, and *n* indicates the number of inorganic slabs in each layer. Particularly compared with Dion Jacobson (DJ) phase perovskite, the thickness of RP phase perovskites can be precisely regulated through additional mechanical exfoliation, enabling the acquisition of very thin layers such as (BA)₂(MA)_{n−1}PbI_{3n+1} with *n* ranging from 1 to 4 from the corresponding bulk single crystals.²⁴ Extensive investigations have been conducted on the light–matter interaction in uniform 2D perovskite crystals, yielding significant advance-

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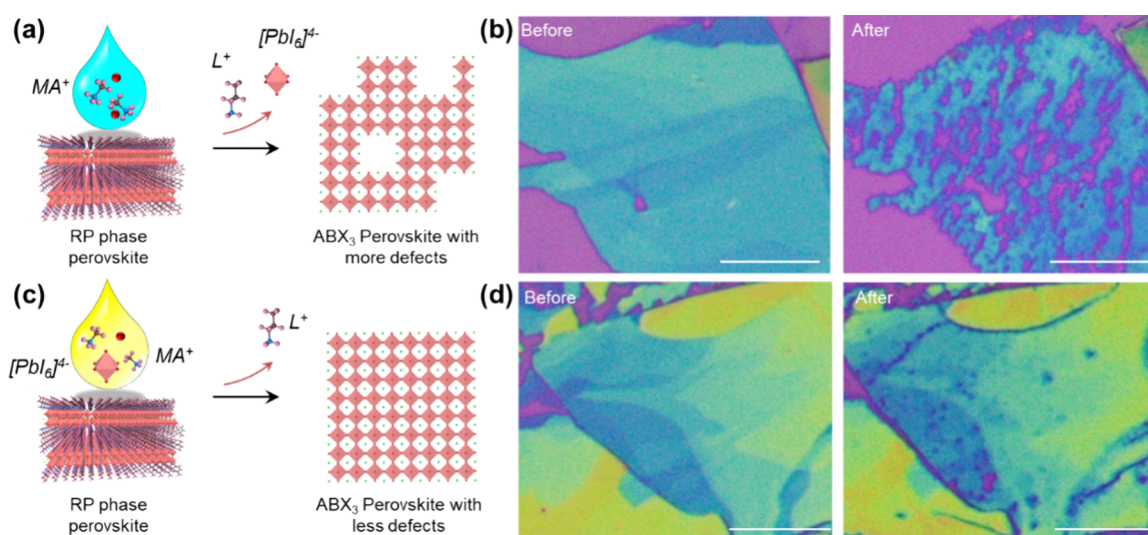


Figure 1. Designed IPA equilibrium solution strategy to realize MAPbI₃ perovskite using 2D RP perovskite as a template. (a) Schematic to show the reaction result by using IPA solution only containing MAI, indicating significant dissolution of perovskites and more defects. (b) Comparison between before (left) and after (right) reaction after 3 min in only MAI IPA solution indicates dissolution of RP phase perovskites. Scale bars are 10 μ m. (c) Schematic to show the reaction result by using MAI/PbI₂ equilibrium solution, indicating the well-preserved structure of perovskite. (d) Comparison between before (left) and after (right) reaction after 15 min in MAI/PbI₂ equilibrium solution indicates less dissolution of RP phase perovskites and good preservation of shape. Scale bars are both 10 μ m.

ments.²⁵ Nevertheless, a comprehensive understanding of the photophysical characteristics at the interface of 2D perovskite vertical junctions is hindered by the absence of direct interfacial electron coupling, which is impeded by the presence of bulky organic ligands.²⁶

Hence, to build the effective heterostructure, there is a requirement to produce extremely thin LD perovskite materials with an exposed intrinsic inorganic surface, a task that is challenging due to the fragile and ionic nature of the structure. By utilizing methylammonium iodide (MAI) or formamidinium iodide (FAI) vapor, lead iodide (PbI₂) nanoplates deposited on substrates have been successfully transformed into MAPbI₃/FAPbI₃ perovskites with high crystalline quality, enabling thickness variations from a few to hundreds of nanometers.^{27–30} However, enhancing the crystal quality of perovskites remains imperative, primarily owing to the elevated temperature necessary for the conversion process. Additionally, the operability within heterostructure fabrication is further hindered by the influence of polar solvents involved in the transfer process. Our recent studies have indicated that 2D RP phase perovskites can act as templates for producing ultrathin MAPbI₃ nanosheets, which can serve as fundamental components for creating vertical junctions.³¹ Nevertheless, the exact conversion mechanism remains incompletely understood. Herein, this research would systematically investigate the dynamic conversion process in the reaction solution, including the transition from the 2D RP phase to the 3D phase, explaining the substitution of small cations (MA⁺) with bulky ligands (L⁺), and the fusion of adjacent inorganic layers. Notably, the thickness of the resulting MAPbI₃ can be controlled by either the thickness (or layer numbers) or the nanometer values of RP phase perovskites. It was observed that enhancing the *n* values of 2D perovskites can improve the crystal quality of ultrathin MAPbI₃, with the high quality being validated through atomic imaging of inorganic layers and organic cations. In addition, by successfully synthesizing ultrathin MAPbI₃ perovskite on diverse substrates, an artificial

twisted MAPbI₃ moiré superlattice was constructed to showcase a vertical junction. High-resolution transmission electron microscopy (HRTEM) distinctly exhibited squared moiré patterns with localized high-symmetry stacking. Through integration with first-principles calculations, it was disclosed that local interlayer coupling can be intensified through moiré potential modulation, resulting in distinctive properties that exhibit promise for future research pursuits.

2. RESULTS AND DISCUSSION

2.1. Equilibrium Solution Design to Realize Ultrathin MAPbI₃ Perovskite Nanosheets. To create MAPbI₃ perovskite microplates/film, a standard procedure involves utilizing a solution of dissolved MAI in isopropyl alcohol (IPA) to interact with a solid-state PbI₂ film.^{32,33} Given the limited solubility of PbI₂ in IPA, this synthesis reaction for perovskites is categorized as a solid–liquid reaction, resulting in the formation of a minor quantity of octahedral [PbI₆]^{4−} in the solution at equilibrium (Figure S1). Upon reaching equilibrium (Formula 1), the concentration of [PbI₆]^{4−} can be approximated by $c([\text{PbI}_6]^{4-}) = K_1 c(\text{I}^-)^4$, where *K*₁ represents the equilibrium constant of the reaction and is of a notably low value. Obviously, the concentration of [PbI₆]^{4−} is significantly influenced by the iodide anion concentration (or MAI concentration). Subsequently, if this “equilibrium solution” comprising MA⁺, I[−], and [PbI₆]^{4−} is employed to process a thin RP phase perovskite crystal, according to our previous results,³¹ it will directly transform the RP perovskite (2D phase) into a MAPbI₃ perovskite (3D phase) by eliminating the ligand cation (L⁺) and releasing excess I[−] from the RP perovskite crystal matrix (Formula 2). It is evident that while MA⁺ is advantageous, I[−] is not conducive to this conversion reaction. Hence, it is postulated that by converting I[−] into [PbI₆]^{4−}, the equilibrium solution contains a higher proportion of MA⁺ compared to I[−], thereby rendering it favorable for the reaction exhibited in Formula 2. Furthermore, if the *in situ* formation of the MAPbI₃ perovskite sheet with a 3D phase is

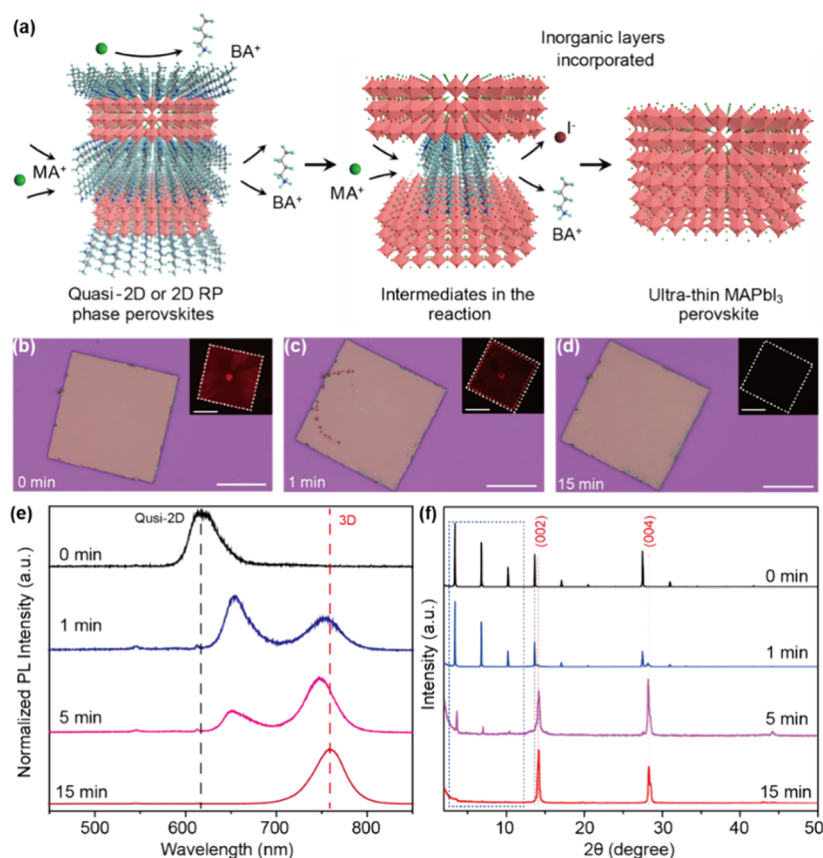
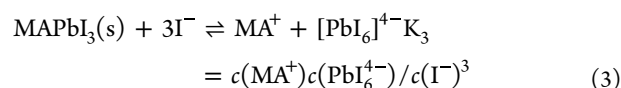
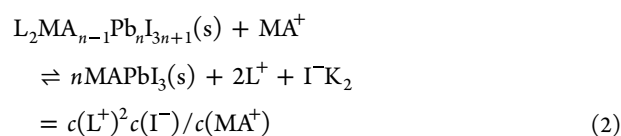
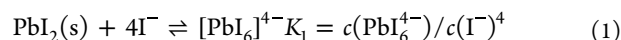


Figure 2. Conversion mechanism based on the MAI/PbI₂ equilibrium solution method. (a) A proposed mechanism to represent the releasing of bulky ligands and insert of MA⁺ cations to form MAPbI₃ perovskite structure. (b–d) A quasi-2D RP phase perovskite nanocrystal, (BA)₂MA₂Pb₃I₁₀, was used to prove the conversion mechanism by tracking the reaction with the time, 0 min (b), 1 min (c), and 15 min (d). The insets are the corresponding PL emission images with the UV–vis detector. All the scale bars are 20 μm. (e) Corresponding PL emission spectra of the perovskite nanocrystal with different reaction times. The small blueshift for increasing the reaction time from 1 to 5 min may originate from the diffusion of more MA⁺ cations into lattice to eliminate lattice defects. (f) XRD characterizations of the perovskites on silicon substrate with different reaction times. The signals marked by rectangles with dashed lines represent the quasi-2D RP phase perovskite, and the red dashed lines represent MAPbI₃ perovskite with a 3D structure.

exceedingly thin, it will be susceptible to dissolution with the assistance of I[−] to generate [PbI₆]^{4−} (Formula 3). Building upon this analysis, it is further conjectured that the presence of [PbI₆]^{4−} in the equilibrium solution may aid in impeding the dissolution of MAPbI₃, consequently resulting in the production of superior quality thin MAPbI₃ crystals. To illustrate this phenomenon, two types of IPA solutions, one containing solely MAI and the other equilibrated by MAI/PbI₂ with the proper ratio, were employed to treat RP phase halide perovskites, as depicted in Figure 1a. It was evident that significant dissolution of RP phase perovskite occurred in the pure-MAI solution after 3 min (Figure 1a,b), whereas the perovskite shape remained intact in the MAI/PbI₂ equilibrium solution even after 15 min (Figure 1c,d). Through complementary photoluminescence (PL) emission analysis (Figure S2), it was observed that the distinctive characteristics of RP phase perovskite vanished following treatment with the equilibrium solution, with the emergence of emission traits specific to MAPbI₃ perovskites. This suggests the complete substitution of bulky ligands with MA⁺ cations within the lattice, which is in agreement with the aforementioned assumption. Consequently, a viable strategy for producing ultrathin MAPbI₃ perovskites through equilibrium solution conversion is reasonably proposed, utilizing 2D or quasi-2D RP phase perovskites as a template.



2.2. Dynamic Conversion Mechanism from 2D Perovskite to 3D Perovskite. To gain a deeper comprehension of the conversion process, a potential dynamic conversion mechanism is further proposed, as depicted in Figure 2a. Once treated with the equilibrium solution, the conversion process involves the initial release of bulky ligands located on the upper surface and in close proximity to the edge of RP phase perovskites due to concentration-induced diffusion. This release of bulky ligands leads to the formation of interlayer channels between the inorganic layers composed of [PbI₆]^{4−} octahedrons, facilitating the smooth diffusion of MA⁺ cations to replenish the vacancies within the lattice. Subsequently, as the bulky ligands are substituted by MA⁺ cations, the inorganic framework with an unaltered surface is exposed, showcasing

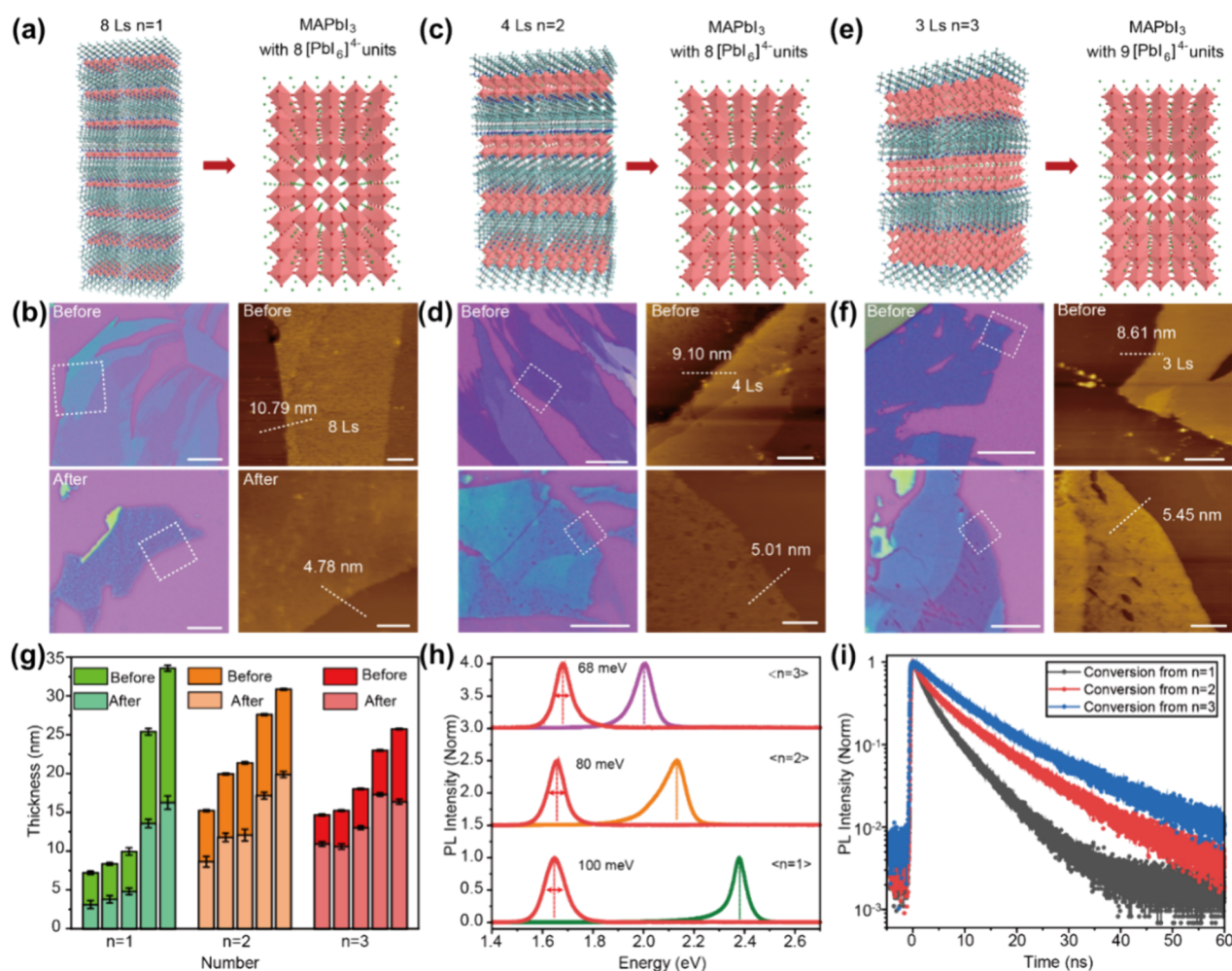


Figure 3. Thickness controlling by different 2D and quasi-2D RP phase perovskites. (a, b) Eight layers (8 Ls) 2D RP phase perovskites ($n = 1$) for conversion to MAPbI₃ perovskites. (c, d) Four layers (4 Ls) quasi-2D perovskites ($n = 2$) for conversion to MAPbI₃ perovskites. (e, f) Three layers (3 Ls) quasi-2D RP phase perovskites ($n = 3$) for conversion to MAPbI₃ perovskites. All the scale bars for optical images are 20 μm and for AFM images are 2 μm . (g) Thickness changes before and after conversion by using different RP phase perovskites with $n = 1, 2$, and 3. (h) Comparison on the PL emission spectra of MAPbI₃ perovskites with a similar thickness (~ 5 nm) converted from different RP phase perovskites with $n = 1, 2$, and 3. (i) Comparison on the corresponding PL lifetime of MAPbI₃ perovskites in panel (h).

the lattice structure as the thinned-MAPbI₃. Moreover, owing to the short distance between the interlayers, the adjacent inorganic layers bond together by sharing an iodide ion (I^-) between two $[\text{PbI}_6]^{4-}$ octahedra and eliminating excess iodide ions. Upon completion of bonding between the layers, a MAPbI₃ structure with an increased thickness is formed. The final thickness of synthesized MAPbI₃ is solely dictated by the quantity of inorganic layers present in the original RP phase perovskite sample. Furthermore, without causing harm to the inorganic frameworks throughout the entire conversion process, the synthesized MAPbI₃ also mirrors the same morphology as that of the original RP phase perovskite.

To rigorously assess the proposed dynamic mechanism, a quasi-2D RP phase perovskite nanocrystal, $(\text{BA})_2\text{MA}_2\text{Pb}_3\text{I}_{10}$, was synthesized utilizing the solution–air interface method³⁴ and subsequently transferred onto a SiO₂ (300 nm)/Si substrate to monitor its temporal evolution (Figure 2b–d). The initial state of the sample, as shown in Figure 2b, exhibited a uniform red emission, as evidenced by the corresponding photoluminescence (PL) spectra with an emission wavelength of approximately 610 nm (Figure 2e), characteristic of quasi-2D RP phase perovskite with $n = 3$. Upon treatment with the

equilibrium solution, a noticeable darkening of the emitting color, particularly pronounced at the edges, was observed (Figure 2c). Analysis of the PL spectra (Figure 2e) revealed a remarkable phenomenon where two new emission peaks, situated at approximately 650 and 740 nm, replaced the original emission peak (~ 610 nm) from the quasi-2D RP phase perovskite. Subsequent detailed characterizations conducted at various positions on the sample (Figure S3) elucidated that the emission peak at ~ 650 nm predominantly emanated from the central portion of the perovskite crystal, while the emission at ~ 740 nm originated from the edge. The former emission can be attributed to the reduction of lattice distortion in the quasi-2D RP phase perovskite structure due to the replacement of bulky ligands (BA^+), despite the unchanged number of inorganic layers, a phenomenon not previously reported.³⁵ The latter emission arises from the incorporation of two adjacent inorganic frameworks devoid of ligands at the edge, leading to their convergence into a thicker 3D structure. This emission could be further enhanced by incorporating more inorganic frameworks with an increased reaction time.

As the reaction progressed, the original red emission color with a shorter wavelength completely disappeared, as

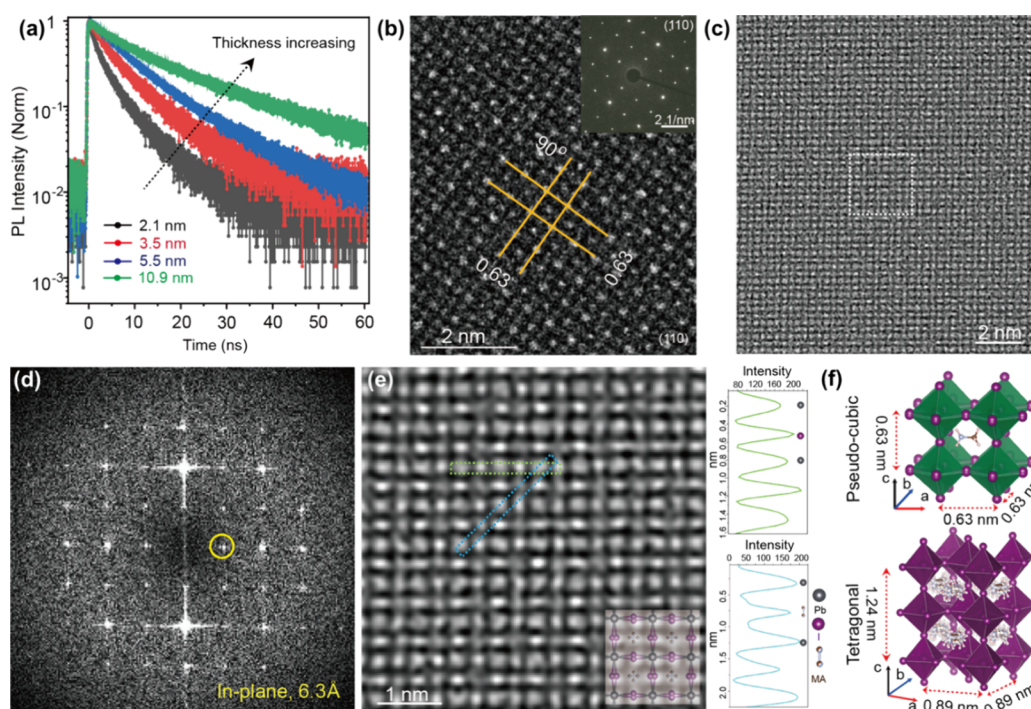


Figure 4. Effect of thickness on lifetime and TEM characterization. (a) PL lifetime of MAPbI₃ perovskite with different thickness, varying from about 2–10 nm. (b) HRTEM image of the obtained MAPbI₃ perovskite with the thickness of about 5 nm. Corresponding SEAD pattern of MAPbI₃ perovskite. (c) Raw phase image retrieved by the single sideband (SSB) ptychographic method. (d) Corresponding Fourier transform of the phase image in panel (c). Yellow circles indicate that the in-plane lattice distance is 6.3 Å. (e) Corresponding enlarged and Wiener filtered image (left) and line profiles along (110) (green) and (200) (blue) directions (right). The inset shows an overlaid structure model indicating the atomic positions. (f) The pseudocubic (Space group *Pm3m*, *a* = 6.3 Å) and tetragonal (Space group *I4/mcm*, *a* = 8.9 Å, *c* = 12.4 Å) structures of MAPbI₃ perovskites with different thicknesses and illustrated by HRTEM data (b–d) and XRD results in Figure S9.

evidenced by the PL image in Figure 2d, indicating the completion of the conversion from quasi-2D perovskite to a 3D structure within 15 min. At this juncture, only one peak, located at approximately 755 nm, was discernible in the PL spectrum, exhibiting a smaller redshift (~15 nm) compared to the peak (~740 nm) observed in the early stages of the reaction (Figure 2e). This shift is attributed to the further increase in thickness resulting from the incorporation of all of the inorganic lead iodide layers in the 2D perovskite. This evolution was supported by the X-ray diffraction (XRD) results shown in Figure 2f, and specifically, the XRD signals exclusively exhibited the characteristic peaks originating from quasi-2D perovskite (*n* = 3) precursors at the initial reaction stage, consistent with reported findings.²⁴ As the reaction progressed, a discernible trend emerged wherein the peaks of quasi-2D RP phase perovskites, particularly those at small angles, gradually diminished, ultimately yielding two characteristic peaks at $2\theta = 14.15$ and 28.40° . These peaks are ascribed to the orderly vertical stacking of octahedral [PbI₆]⁴⁻, confirming the formation of a 3D structure in the final converted products. Collectively, all results furnish unequivocal evidence of the successful conversion of 2D or quasi-2D perovskites to MAPbI₃ with a 3D structure.

2.3. Thickness Controlling Strategy and Structure Properties. It is noteworthy that all the 2D RP phase perovskites with varying *n* values (*n* = 1, 2, and 3) can serve as templates for achieving the MAPbI₃ perovskite structure using the equilibrium solution conversion method. This presents a viable approach for regulating the thickness of MAPbI₃ by adjusting the nanometer values and layer numbers of RP phase perovskites. For instance, as illustrated in Figure 3a–f, MAPbI₃

perovskites with a comparable thickness of approximately 5 nm, as determined by atomic force microscopy (AFM), were successfully obtained utilizing RP phase perovskites with *n* = 1 (8 layers), *n* = 2 (4 layers), and *n* = 3 (3 layers), respectively. Notably, the most significant variation in thickness between pre- and postconversion was observed in the RP phase perovskites with *n* = 1, likely attributed to the presence of bulky ligands within the lattice of RP phase perovskites, particularly pronounced in *n* = 1 perovskite. Intriguingly, further analysis (Figure 3g) of the thickness alterations of RP phase perovskites pre- and postconversion suggests a consistent ratio for different perovskite samples with the same RP phase, namely, 57% for *n* = 1, 41% for *n* = 2, and 29% for *n* = 3. These consistent ratios closely align with the occupancy of bulky ligands in the respective original RP phase perovskites with different *n* values (refer to Table S1), indicating no loss of the inorganic layers during the conversion process. Moreover, additional assessments of steady-state PL in Figure 3h also confirm the successful conversion, albeit revealing slight discrepancies in the emission peak positions, ranging from 755 nm for *n* = 1–745 nm for *n* = 3. Given the diminished confinement effect with increased thickness, the minor variation in thickness between the two samples acquired from RP perovskites with different *n* values is not the primary cause of this discrepancy in emission peak. Instead, defects are commonly considered to be the pivotal factor influencing the optical characteristics of perovskites by trapping excitons/carriers. Hence, this discrepancy can be attributed to the structural defect, including vacancy, interfacial merging, and lattice stretching. Furthermore, the broadened full width at

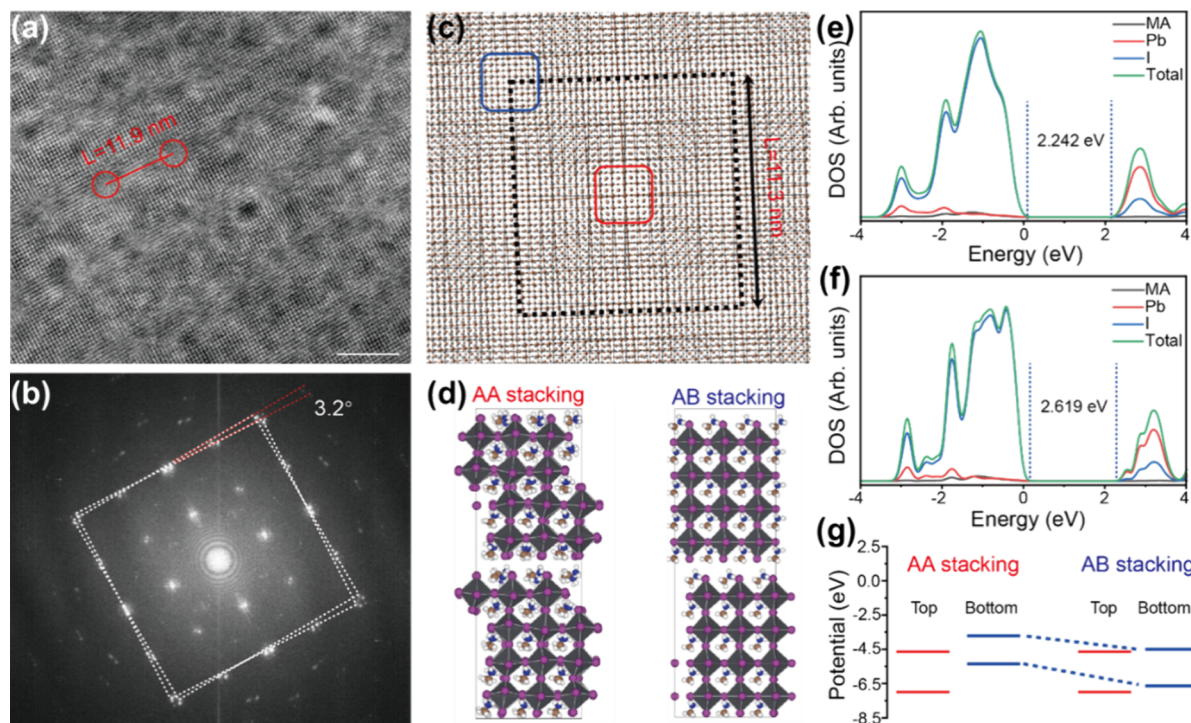


Figure 5. Moiré superlattice formed by twisted bilayers of MAPbI₃ perovskite nanosheets. (a) Moiré pattern and its periodicity of twisted bilayers of MAPbI₃ perovskite nanosheets indicated by the HRTEM. The scale bar is 10 nm. (b) Selected area electron diffraction measurements for the region of panel (a). Two sets of diffraction spots and a formed intersection angle of 3.2° indicate that bilayer MAPbI₃ nanosheets are twisted by 3.2°. (c) Perpendicular view of the simulated bilayer MAPbI₃ nanosheets with the twist angle of 3.2°, forming a moiré superlattice with periodicity $L = 11.3$ nm. To clearly demonstrate the moiré pattern, a simplified and squared lattice was used. (d) Two distinct localized stacking structures observed in panel (c), AA-stacking (left) and AB-stacking (right). (e, f) Calculated density of states for AA-stacking (e) and AB-stacking (f) to show different band gaps for the localized structures. (g) The band alignment of localized stacking configurations in AA-stacking and AB-stacking obtained by first-principles calculations.

half-maximum (fwhm) of the peak at the 755 nm wavelength also supports this explanation.

The analysis presented above suggests that the MAPbI₃ sample containing $n = 1$ RP phase perovskite exhibits more defect species, as illustrated in Figure 3h. It is indicated that the defect species of the as-synthesized MAPbI₃ perovskites could be reduced by increasing the n values of RP phase perovskites. To support this interpretation, the charge carrier dynamics of three distinct MAPbI₃ perovskites of similar thickness were compared by analyzing time-resolved PL (TRPL) spectra at the primary steady-state PL peak (~ 755 nm), which reflects the defect density. The results depicted in Figure 3i reveal a correlation between the PL lifetimes of the final MAPbI₃ perovskites and the n values of the corresponding RP phase perovskite precursors, with larger n values leading to longer lifetimes when excited by a 447 nm laser under a power of 50 nW. Typically, the presence of certain defects offers an additional pathway for exciton recombination, resulting in shorter lifetimes. Therefore, the observed trend of carrier lifetime variations with changes in n values aligns with the aforementioned interpretation. To gain a deeper understanding of the impact of n values on the defect density of the synthesized MAPbI₃ perovskites, schematics presented in Figure 3a,c,e are utilized to compare the conversion process. During this process, it is necessary to employ more layers of RP phase perovskites with lower n values, such as $n = 1$, to achieve the same thickness, thereby increasing the number of interfaces involved. This scenario enhances the likelihood of introducing defect species and density during the removal of

ligands in the perovskite matrix, particularly I-vacancies and imperfect interfacial merging. Conversely, high-quality MAPbI₃ perovskite is obtained by utilizing 2D perovskites with higher n values, as they involve fewer interface mergers and exhibit intrinsic stacking closer to that of MAPbI₃ perovskites. Similarly, decreasing the bulky BA⁺ cation concentration has the same function as increasing the n value of RP phase perovskites to improve the defect density of the as-synthesized MAPbI₃ nanosheets.

Meanwhile, the PL lifetimes depicted in Figure 4a exhibit a gradual prolongation with increasing thickness, consistent with findings in the literature.³⁶ The intricate structure of the resulting ultrathin MAPbI₃ perovskite nanosheets was further scrutinized using transmission electron microscopy (TEM). Employing a physical transfer system in conjunction with optical microscopy, the ultrathin MAPbI₃ perovskite nanosheets, synthesized directly on polydimethylsiloxane (PDMS), were transferred onto SiN_x TEM grids with a thickness of approximately ~ 5 nm. It is well-known that hybrid perovskites are prone to rapid degradation under electron-beam irradiation, posing significant challenges for TEM characterization, particularly with the synthesized ultrathin sample thickness ranging between 1.2 and 2.4 nm, consisting of only 2-to-4 [PbI₆]⁴⁻ octahedron layers. To mitigate the beam damage issue, a low electron dose, specifically $15 \text{ e}^- \text{Å}^{-2}$ (e^- denoting electrons), was adopted for acquiring high-resolution TEM (HRTEM) images and selected area electron diffraction (SAED) patterns. As depicted in Figure 4b, the HRTEM image displays equal lattice parameters (a and b) in the plane,

both measuring 0.63 nm.³⁷ The 4-fold in-plane symmetry was corroborated by the SAED patterns, with the absence of diffuse scattering points indicating a single crystal nature of high quality.

To elucidate the atomic arrangement of the ultrathin MAPbI₃ perovskite further, 4D scanning transmission electron microscopy (4D-STEM) was employed. However, in the conventional high-angle annular dark field (HAADF) STEM, sensitive to atomic number distributions, the signal of MA⁺ is always absent due to the weak scattering of light carbon and nitrogen atoms by the electron beam, resulting solely in the observation of heavy atoms, lead (Pb) and iodine(I), within a tetragonal perovskite structure (Figure S8). In contrast, the ptychographic single sideband (SSB) method, being dose-efficient and easily interpretable, facilitated the phase retrieval of both light and heavy atoms in MAPbI₃, enabling simultaneous imaging with an annular detector.³⁸ As exhibited in Figure 4c, all atomic columns are discernible in the phase image, including the lightest MA⁺ molecules. The corresponding Fourier transform image (Figure 4d) indicates a higher resolution than the HAADF image (Figure S8), revealing a clear Pb–I–Pb lattice with an interplanar spacing of 6.3 Å, consistent with HRTEM results (Figure 4b), owing to the high dose efficiency of the SSB method that utilizes more electrons for imaging than HAADF STEM. Moreover, the positions of MA⁺ cations, I and Pb atoms are clearly distinguishable in the profile of the atomic columns (Figure 4e), identified by their distinct peaks. Particularly, the denoised phase image presented in Figure 4e provides further insight into the intact structure of the ultrathin MAPbI₃ nanosheet, revealing elliptical contrasts of iodine columns, suggesting a tilt angle between the upper and lower layers of [PbI₄][−] octahedrons. Additionally, the lack of a fixed shape of MA⁺ molecules may be attributed to the random orientations of rotated MA⁺ cations within the cubic cage formed by Pb²⁺ at room temperature. To comprehend the crystal stacking structure better, parameter *c*, involving the out-of-plane stacking spacing, was extracted from the XRD results. An intriguing observation is the dependence of XRD results on sample thickness, resulting in two distinct sets of diffraction peaks (Figure S9). For thin samples (thickness <20 nm), the diffraction peak occurs at $2\theta = 14.00^\circ$, while for thick samples (thickness >20 nm), it shifts to $2\theta = 14.15^\circ$. With Bragg's Law ($d = \lambda/2\sin\theta$), the distances of adjacent faces were calculated as 0.63 nm for thin samples and approximately 0.62 nm for thick samples. It can be inferred that the thin sample exhibits a pseudocubic phase (Space group *Pm3m*) with parameters $a = b = c = 0.63$ nm (Figure 4d), while the thick sample belongs to a tetragonal phase (Space group *I4/mcm*, $a = 8.9$ Å, $c = 12.4$ Å) as illustrated in Figure 4e. The peaks near 14° are attributed to (001) for the pseudocubic phase and (002) for the tetragonal phase, respectively. This discrepancy may originate from substrate-induced strain, which would significantly affect the vertical stacking spacing for ultrathin MAPbI₃.

2.4. Artificial Twisted MAPbI₃ Moiré Superlattice and Localized Properties. To illustrate homojunctions within thin MAPbI₃ perovskite nanosheets, an artificial twisted superlattice was created by using a physical transfer process. In this process, ultrathin MAPbI₃ nanosheets, each with a thickness of less than 5 nm, were meticulously stacked layer-by-layer along the *c*-axis direction. Subsequently, the twisted superlattice was observed by using high-resolution transmission electron microscopy (HRTEM), as depicted in Figure

5a. In contrast to the single sheet of as-synthesized ultrathin MAPbI₃ in Figure 4b, the twisted superlattice exhibits distinct squared moiré patterns with a period length (*L*) of 11.9 nm. Additionally, the corresponding selected area electron diffraction (SAED) pattern of the moiré superlattice in Figure 5b clearly reveals two sets of diffraction spots with an intersection angle of approximately 3.2° , indicating a twist between adjacent sheets of this magnitude. This phenomenon resembles the formation of moiré superlattices observed in twisted graphene or transition-metal dichalcogenides (TMDCs) bilayers.^{39,40} Furthermore, a simulated image in Figure 5c was generated using a simplified lattice to represent the top and bottom layers, respectively, accurately replicating the moiré patterns observed in Figure 5a. Moreover, in the context of vertical homojunctions, the precise period (*L*) of such moiré superlattices is determined by the equation $L = a_0/\sin\theta$,⁴¹ where *a*₀ represents the distance (0.63 nm) of the in-plane Bravais lattice and θ denotes the twist angle. Consequently, the theoretically calculated period (*L*) is 11.3 nm (Figure 5c), with *a*₀ being 6.3 Å for ultrathin MAPbI₃, directly obtained from the TEM image in Figure 4b. This value aligns well with the measurement in Figure 5a, despite the stacked ultrathin MAPbI₃ perovskite nanosheet not being an atomic monolayer.

Additionally, the simulated image in Figure 5c reveals the presence of at least two distinct types of localized orderly stacking patterns, hereafter referred to as AA-stacking and AB-stacking (corresponding to AA and HH stacking, respectively, in ref 40, which presents a similar square lattice), as depicted in Figure 5d, within the moiré structures at the atomic scale. These patterns have been anticipated in a prior literature,⁴² with AB-stacking typically demonstrating greater energetic stability owing to potential interlayer H bonds, while AA-stacking tends to be less stable. Consequently, unconventional properties may manifest and be delineated through moiré potential. Utilizing the models in Figure 5d, we used density functional theory (DFT) computations to determine the electronic density of states (DOS) for the two localized stacks and extracted their corresponding band gaps as illustrated in Figure 5e,f. In comparison with bulk MAPbI₃ perovskite (Figures S10 and S11), both localized stacking structures exhibit an augmentation in the band gap. However, the augmentation is more pronounced in AB-stacking due to the substantial reconstruction induced by interlayer H bonds. The notable dependence of the band gap on the localized position could result in a spatial modulation of the electronic structure and associated properties. We further computed the relative electronic band edges of the top and bottom layers using an electrostatic potential alignment method. As depicted in Figure 5g, a type-II band alignment would potentially emerge in AA-stacking, likely due to interface distortion with repulsion from I–I contact, thereby yielding the possibility of interlayer excitons. Meanwhile, the formation of hybridized excitons in AB-stacking arises from its pseudotype-II band alignment. This suggests that the excitonic properties of perovskite vertical junctions can be manipulated by the twist angles and the coexistence of various local stacking configurations, akin to those of other 2D materials.

3. CONCLUSIONS

In summary, we provide reasonable explanation of how we achieve an equilibrium solution to produce ultrathin MAPbI₃ perovskite nanosheets with precise thickness control and

exposed intrinsic surfaces. This is accomplished by utilizing a 2D RP phase perovskite as a template. Based on the analysis of species under reaction equilibrium, the critical aspect enabling this successful transformation involves establishing a reaction environment containing a minimal quantity of octahedral $[\text{PbI}_6]^{4-}$, which hinders the dissolution of the inorganic frameworks of perovskites. Furthermore, the thickness of MAPbI_3 can be effectively regulated by adjusting the n values or inorganic layer numbers within the 2D RP phase perovskite template. Moreover, an increase in the n value also aids in reducing the defect density of the synthesized ultrathin MAPbI_3 perovskite by minimizing the interfacial merging of inorganic frameworks. As an illustration, we constructed an artificial moiré superlattice with a twist angle of 3.2° using the high-quality ultrathin MAPbI_3 perovskite. The resulting moiré pattern displays various localized stacking structures with notable symmetry. Through complementary first-principles calculations, it is revealed that the local interlayer coupling can be strengthened through moiré potential modulation, leading to distinctive properties that warrant further exploration. Our discoveries introduce a novel approach for fabricating ligand-free ultrathin perovskite nanosheets and establish a foundation for investigating photophysics related to interfacial coupling in emerging low-dimensional material systems.

4. EXPERIMENTAL SECTION

4.1. Chemicals and Materials. Solvents, including anhydrous chlorobenzene (CB), isopropyl alcohol (IPA), hydroiodic acid (HI, 57 wt % in H_2O), hypophosphorous acid (H_3PO_2 , 50 wt % in H_2O), and solid chemicals including PbO powders and lead iodide (PbI_2) were purchased from Sigma-Aldrich. n -Butylammonium iodide (BAI) and methylammonium iodide (MAI) were purchased from Greatcell Solar Ltd. All chemicals were used as received.

4.2. Synthesis of 2D and Quasi-2D Perovskite Single Crystals. For the BA_2PbI_4 crystal, PbO (0.57 mmol) and BAI (0.57 mmol) precursors were used. For $\text{BA}_2\text{MAPb}_2\text{I}_7$ crystal, PbO (0.59 mmol), BAI (0.43 mmol), and MAI (0.31 mmol) precursors were used. For $\text{BA}_2\text{MA}_2\text{Pb}_3\text{I}_{10}$ crystal, PbO (0.59 mmol), BAI (0.19 mmol), and MAI (0.4 mmol) precursors were used. To grow each crystal, all the precursors were dissolved into an acid mixture containing 0.9 mL of HBr or HI and 0.1 mL of H_3PO_2 in a 10 mL glass vial and heated to 120°C in an oil bath [ref S1, Supporting Information]. Once the precursors were completely dissolved, the stirring was terminated and the solution was cooled to room temperature with a cooling rate of $10^\circ\text{C}/10\text{ min}$. The crystals were collected by vacuum filtration.

4.3. Conversion from 2D Perovskites to MAPbI_3 Perovskite Using the Equilibrium Solution Method. The equilibrium solution was made by PbI_2 (10 mg)/MAI (10 mg) in 1 mL of IPA solution. To reach equilibrium, the solution was heated at 40°C on a hot plate for overnight. Then, 250 μL of supernatant of equilibrium solution was used for conversion at room temperature, and reaction times were 1, 5, and 7 min to acquire thin MAPbI_3 perovskites from exfoliated BA_2PbI_4 , $\text{BA}_2\text{MAPb}_2\text{I}_7$, and $\text{BA}_2\text{MA}_2\text{Pb}_3\text{I}_{10}$ precursors on the silicon substrate, respectively. The reaction was performed in a 4 mL glass vial. After reaction, the samples were washed by 1 mL of CB and IPA mixed solution with the volume ratio of 100/3 and further annealed at 55 – 58°C for 10 min.

4.4. Optical Characterizations. The optical images were collected by a custom microscope (Olympus BX53). The photoluminescence images were collected under the excitation of a light source (012-63000; X-CITE 120 REPL LAMP). The filter cube contains a bandpass filter (330–385 nm) for excitation and a dichroic mirror (cutoff wavelength, 400 nm) for light splitting and a filter (long pass 420 nm) for emission. The photoluminescence spectra were collected by a spectrometer (SpectraPro HRS-300). The time-resolved PL measurements were carried out using a 40x [numerical

aperture (NA), 0.60] objective in a home-built microscope setup with a laser light generated by a picosecond-pulsed diode (LDH-P-C-450B, PicoQuant), pumping at 2.8 eV (full width at half-maximum, 50 ps).

4.5. Atomic Force Microscopy Images. Cypher ES Environmental AFM was used for the measurement with probe-type AC240TM-R3. During the imaging, the tapping mode was used.

4.6. XRD Measurements. XRD was measured using a powder X-ray diffractometer (Panalytical Empyrean) with a $\text{Cu K}\alpha$ source. The wavelength (λ) is 0.154 nm. The XRD measurements were performed on the as-grown MAPbI_3 perovskites covering almost the entire surface of the SiO_2 (300 nm)/Si substrate. For thin samples, the 2D perovskite precursors were further exfoliated several times after being transferred onto silicon substrates. To do XRD measurements on thin and thick samples, the conversion reaction was conducted in 1 mL equilibrium solution for 1 h to ensure all the precursors are converted to MAPbI_3 .

4.7. TEM Characterization for the Single-Layer MAPbI_3 Nanosheet and Twisted Structure. To acquire the high-resolution transmission electron microscopy (HRTEM) image, the ultrathin MAPbI_3 nanosheet was directly synthesized on polydimethylsiloxane (PDMS) substrate and then transferred onto SiN_x TEM grid with the thickness of 5 nm. The 4D-STEM data sets were acquired using an event-driven Timepix3 direct electron camera equipped on probe aberration-corrected Thermo Fisher Advan-TEM. The accelerating voltage was 200 kV, and the convergence angle was set to 13 mrad. The collection angle of HAADF image was 48–200 mrad. The probe current was less than 0.2 pA, and the dwell time was 0.5 μs . The 4D data sets were processed using the single sideband (SSB) method of 558 ptychography with a homemade python code. For the twisted MAPbI_3 structure, the MAPbI_3 nanosheet was transferred twice, and the twist angle was controlled by the optical transfer system.

4.8. Computational Details. DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP), [refs S2–S4, Supporting Information] applying the projector augmented wave (PAW) pseudopotentials [ref S5, Supporting Information] and the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) [ref S6, Supporting Information] for the exchange–correlation energy. For all calculations, the kinetic energy cutoff for the plane-wave basis was set to 500 eV. The Brillouin zone was sampled based on a Monkhorst–Pack k-point mesh, with a reciprocal mesh of $6 \times 6 \times 6$ for the MAPbI_3 cubic unit cell (with an optimized pseudocubic lattice constant of $\sim 6.3\text{ \AA}$) and a $2 \times 2 \times 1$ mesh for homojunction structures. For geometry optimization, the force convergence threshold was set to be $-0.025\text{ eV/\AA}$ and the self-consistent energy convergence threshold is 10^{-6} eV . DFT-D3 correction was applied along with GGA-PBE in all calculations to account for vdW interactions [ref S7, Supporting Information]. The electronic band structure was calculated at high-symmetry k-point paths, which is G (0,0,0), X (0.5,0,0), M (0.5,0.5,0), and R (0.5,0.5,0.5) for the cubic phase. Figures S10 and S11 show DFT-optimized crystal structures and computed band structures for the cubic and tetragonal phases of MAPbI_3 . The MAPbI_3 homojunction structures were built from DFT-optimized layered MAPbI_3 . A $3 \times 3 \times 2$ (001) MAPbI_3 slab was used to construct the bottom and top layers of the bilayer structure, and necessary horizontal displacements were performed to model the AB- and AA-stacking configurations. Electronic band edges were calculated based on a well-known average electrostatic potential alignment scheme involving bulk, surface slab, and interface calculations [refs S8 and S9, Supporting Information].

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.4c10298>.

Images of solutions with different compositions, optical images of samples tracked with reaction time, more AFM images of the reaction tracked with different thickness, comparison of XRD results between thin and

thick samples, calculated results of bulk MAPbI₃, and crystal parameters of 2D perovskites (PDF)

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Notes

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