Organic-inorganic hybrid perovskites, which have proved to be promising semiconductor materials for photovoltaic applications, have been made into atomically thin two-dimensional (2D) sheets. We report the solution-phase growth of single- and few-unit-cell-thick single-crystalline 2D hybrid perovskites of (C4H9NH3)2PbBr4 with well-defined square shape and large size. In contrast to other 2D materials, the hybrid perovskite sheets exhibit an unusual structural relaxation, and this structural change leads to a band gap shift as compared to the bulk crystal. The high-quality 2D crystals exhibit efficient photoluminescence, and color tuning could be achieved by changing sheet thickness as well as composition via the synthesis of related materials.

**NANOMATERIALS**

**Atomically thin two-dimensional organic-inorganic hybrid perovskites**

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Organic-inorganic hybrid perovskites, which have proved to be promising semiconductor materials for photovoltaic applications, have been made into atomically thin two-dimensional (2D) sheets. We report the solution-phase growth of single- and few-unit-cell-thick single-crystalline 2D hybrid perovskites of (C4H9NH3)2PbBr4 with well-defined square shape and large size. In contrast to other 2D materials, the hybrid perovskite sheets exhibit an unusual structural relaxation, and this structural change leads to a band gap shift as compared to the bulk crystal. The high-quality 2D crystals exhibit efficient photoluminescence, and color tuning could be achieved by changing sheet thickness as well as composition via the synthesis of related materials.

The organic-inorganic hybrid perovskites, especially CH3NH3PbI3, have recently been used in solution-processable photovoltaic devices that have reached 20% power conversion efficiency (1–4). These layered materials have a general formula of (RNH3)2MnX6 (RNH3)2MnX6m, where R is an alkyl or aromatic moiety, A is a metal cation, and X is a halide. The variable m indicates the number of the metal cation layers between the two layers of the organic chains (5–11). In the extreme case where m = ∞, the structure becomes a three-dimensionally bonded perovskite crystal with a structure similar to BaTiO3. In the opposite extreme where m = 1, the structure becomes an ideal quantum well with only one atomic layer of AX2 separated by organic chains, in which the adjacent layers are held together by weak van der Waals forces.

This arrangement is fundamentally different from transition metal dichalcogenides, in which one layer of the metal ions is sandwiched between two hexagonal layers of S or Se atoms, affording a rigid backbone. In contrast, the layered hybrid perovskites normally have a tetragonal or orthorhombic structure and are inherently more flexible and deformable (5–11). By varying the value of m, the thickness and the related optoelectronic properties of the quantum well can be tuned. To date, many organic amines, metal cations (Cu2+, Mn2+, Cd2+, Ge2+, Sn2+, Pb2+, Eu2+, etc.) and halides (Cl, Br, and I) have been used to construct such layered materials (m = 1 ~ 3), and their corresponding optoelectronic properties have been well studied (12–15). Previous reports have claimed that the organic layers effectively isolate the two-dimensional (2D) quantum wells in each layer from electronic coupling, if the organic chain is longer than propyl amine (16). This means that the properties of the atomically thin 2D quantum well should be the same as those of the bulk layered material (microporous crystal, powder, or film). This hypothesis, as well as the technical difficulty of separating individual layers, has probably delayed investigation of free-standing single layers of such 2D materials. Very recently, attempts to obtain ultrathin perovskite samples by spin coating, chemical vapor deposition, or mechanical exfoliation methods have been made with limited success (17–19).

Here we report the direct growth of atomically thin 2D hybrid perovskites [(C4H9NH3)2PbBr4] and derivatives from solution. Uniform square-shaped 2D crystals on a flat substrate with high yield and excellent reproducibility were synthesized by using a ternary co-solvent. We investigated the structure and composition of individual 2D crystals using transmission electron microscopy (TEM), energy-dispersive spectroscopy (EDS), grazing-incidence wide-angle x-ray scattering (GIWAXS), and Raman spectroscopy. Unlike other 2D materials, a structural relaxation (or lattice constant expansion) occurred in the hybrid perovskite 2D sheets that could be responsible for emergent features. We investigated the optical properties of the 2D sheets using steady-state and time-resolved photoluminescence (PL) spectroscopy and cathodoluminescence microscopy. The 2D hybrid perovskite sheets have a slightly shifted band edge emission that could be attributed to the structural relaxation as well as wide composition and color tunability. A structural illustration of a monolayer 2D perovskite (Fig. 1A) shows the case with six Br atoms surrounding each Pb atom, and the four in-plane Br atoms are shared by two octahedrons, forming a 2D sheet of PbBr2. The negative charges are compensated for by the butylammonium that caps the surfaces of the 2D sheet. This structure is amenable to facile solution synthesis. The ionic character of such materials is stronger than the transition metal disulfides and diselenides, and the bulk solid is soluble in polar organic solvents such as dimethylformamide (DMF) (20). To grow 2D sheets, a very dilute precursor solution was dropped on the surface of a Si/SiO2 substrate and dried under mild heating [see the supplementary materials (21)]. A DMF and chlorobenzene (CB) co-solvent was initially investigated, because CB helps to reduce the solubility of (C4H9NH3)2PbBr4 in DMF and promote crystallization. Because CB has a similar boiling point and evaporation rate as DMF, the drying of the solvents and the crystallization process were uniform across the whole substrate.

We examined the products of this reaction by optical microscopy and atomic force microscopy (AFM), but instead of monolayers, thick particles with random shapes formed on the substrate (Fig. S1). Hybrid perovskites have limited solubility in acetonitrile, and the solvent has been used previously for making microscopic hybrid perovskite single crystals (22). In this case, acetonitrile evaporates more quickly and helps induce the formation of the ultrathin 2D hybrid perovskite sheets. When acetonitrile was combined with DMF and CB, uniform square sheets grew on the substrate (Fig. 1B). The edge length of the square crystals ranged from 1 to 10 μm, with an average of 4.2 μm (the size distribution statistics can be found in fig. S2). The detailed synthetic procedure and discussion of the role of each solvent can be found in the supplementary text (27).
The thickness of the square sheets was quantified with AFM. The thickness of the crystals varied from a few to tens of nanometers; the thinnest sheets were ~1.6 nm (±0.2 nm). The AFM images of several monolayer and double-layer sheets show thicknesses of 1.6 and 3.4 nm (±0.2 nm) (Fig. 1, C and D), whereas the d spacing in the bulk crystal was 1.4 nm (20). Unfortunately, the majority of the products from mechanical exfoliation were very thick flakes (fig. S5A) and from solvent exfoliation they were randomly shaped particles (fig. S5, B and C). The monolayer-thick particles obtained were very small (less than 1 μm), which suggests that these hybrid perovskite layers are mechanically brittle.

To determine the crystal structure of the 2D hybrid perovskites, x-ray diffraction (XRD) and TEM were used. The XRD pattern revealed that the (001) plane grew parallel to the substrate, and the out-of-plane d spacing was 1.42 nm (fig. S6), which is consistent with reported data for this material (26). The in-plane structural information was revealed by selected-area electron diffraction (SAED) in a TEM. Figure 2A shows a TEM image of a 2D sheet grown on a lacy carbon grid. After examining more than 20 individual sheets by TEM, we found that they all showed similar shape and identical diffraction patterns (additional TEM images are shown fig. S7); Fig. 2B shows the SAED pattern of another sheet. The calculated average in-plane lattice constants are a = 8.41 Å and b = 8.60 Å from five sheets, which are slightly greater than the lattice constants in the bulk crystal measured by single-crystal XRD (a = 8.22 Å and b = 8.33 Å; see (15) and tables S1 and S2). The electron diffraction patterns were consistent with structural simulations, which further confirm the structure of the atomically thin 2D sheets (see figs. S8 and S9 for more discussion on the simulations/experiments on the bulk and few-layer hybrid perovskites).

We observed rapid radiation damage of the sheets under the strong electron beam. After exposing the 2D sheets to the electron beam for a few seconds, Pb was reduced and precipitated, which caused the sample to be irreversibly damaged (fig. S10). This phenomenon is similar to that observed in alkali halides (24). More examples of SAED patterns of individual sheets and their corresponding TEM images demonstrating the degradation can be found in fig. S11. Figure 2, C to F, shows the elemental distribution in the thin sheets; lead, bromine, carbon, and nitrogen are all present in the square.

The lattice expansion in the 2D sheets was further confirmed through macroscopic GIWAXS measurements. Figure 2G shows the GIWAXS image and Fig. 2H shows the integrated pattern. In addition, to the (200) and (020) peaks observed in TEM diffraction, many other peaks can be assigned. The d spacing of the (200), (020), (111), and (113) planes is 4.19 Å (lattice constant a = 8.38 Å), 4.25 Å (lattice constant b = 8.50 Å), 5.81 Å, and 5.00 Å, respectively. These values are all greater than those of the bulk crystals and are consistent with our TEM measurements of single 2D sheets.

In addition, we examined the Raman spectra of the bulk crystal and the thin sheet as shown in fig. S12. The peaks found at 57.7 and 43.6 cm−1 for the bulk crystal shifted to 55.2 and 41.3 cm−1 for the 2D sheet, respectively. These peaks can be attributed to Pb-Br stretching and librational motions of both inorganic and organic ions (25), indicating that relaxation of the crystal lattice occurs in the thin sheets. Meanwhile, the peak at 122.2 cm−1 (from -CH3 group torsional motion and insensitive to lattice distortion) did not change. The peaks for the 2D sheet became narrower, suggesting better-defined vibrational states in the thin sheet. Furthermore, our density functional theory (DFT) calculation indicates a small lattice expansion of around 0.1 Å for the monolayer as compared to the bulk (C4H9NH3)2PbBr4 crystal (see the supplementary materials for details about DFT simulation).

Strong crystal lattice distortions are common for hybrid perovskites (5–10). Structural distortion–induced optical and electronic changes have been reported in bulk hybrid perovskites (26–29). Single-crystal XRD data of the bulk crystal of (C4H9NH3)2PbBr4 revealed that the PbBr2− layer in the bulk crystal is highly distorted, with a
The direct growth of atomically thin sheets overcomes the limitations of the conventional exfoliation and chemical vapor deposition methods, which normally produce relatively thick perovskite plates (17–19, 32, 33). In contrast to other 2D materials, the structural framework of (C4H9NH3)2PbBr4 ultrathin 2D sheets using similar methods, and their PL spectra and optical images are shown in Fig. 4 (see fig. S16 for XRD and fig. S17 for AFM images). For the (C4H9NH3)2PbBr4 sheet (i), the band edge emission was in the ultraviolet at ~340 nm, which was beyond our detection range for the single-sheet measurement. Three states in the visible region were observed at 486, 568, and 747 nm, which made the sheets appear nearly white. This emission is attributed to the transient formation of self-trapped excitons (31). For the (C4H9NH3)2PbI4 sheet (iii), the band edge emission was at 514 nm, which is blue-shifted by 9 nm as compared to the bulk (5). This blue shift is consistent with the bromide case (ii) discussed above. For the chloride-bromide alloy (v) showed only one peak at 505 nm. In contrast to (C4H9NH3)2(CH3NH3)Pb2Br7, no well-defined squares were observed, and the thickness of the plates was ~10 nm. Preliminary PL study indicates a band edge emission at 453 nm, and a broad self-trapped exciton emission appeared at lower wavelength. However, the bromide-iodide alloy (v) showed only one peak at 505 nm. In the case of (C4H9NH3)2(CH3NH3)PbBr3, no well-defined squares were observed, and the thickness of the plates was ~10 nm. Preliminary PL study indicates a band edge emission at 453 nm, which is red-shifted slightly as compared to the bulk. These results indicate that the 2D hybrid perovskites have excellent composition and color tunability.

The chemistry of synthesizing these ultrathin 2D sheets was extended to other hybrid perovskites (5). We prepared (C4H9NH3)2PbCl4, (C4H9NH3)2PbI4, (C4H9NH3)2PbCl2Br2, (C4H9NH3)2PbBr2I2, and (C4H9NH3)2(CH3NH3)PbBr7 ultrathin 2D sheets with excellent lateral resolution, was used to determine the spatial distribution of emissive sites on the 2D sheets. As shown in Fig. 3G, the cathodoluminescence mapping from 395 to 435 nm shows a square shape identical to the corresponding scanning electron microscopy (SEM) images as shown in Fig. 3F, indicating that the emission is from the whole square. The PL internal quantum efficiency (QE) of the 2D sheets was estimated by comparing the integrated PL intensity (from 390 to 450 nm) of the band edge emission at room temperature (298 K) and helium cryogenic temperature (6 K), and the results are shown in Fig. 3H (30). There is a small red shift of the main peak from 406 to 412 nm as the temperature decreases. The emission at 421 nm (2.91 eV) at 6 K is known from the ground state, which cannot be distinguished from the Γ1 state at room temperature (26). The PL QE for the 2D sheet is calculated to be ~26%, which is much higher than the QE of the bulk crystal (~1%), indicating the high quality of the single-crystalline 2D sheets. The PL intensity increased linearly as the excitation power increased (fig. S15), suggesting that the PL QE was constant within our measurement range. The PL lifetime of the 2D sheets was measured by time-resolved PL. As shown in Fig. 3I, the decay curve showed a bi-exponential feature with lifetimes of 0.78 ns (67%) and 3.3 ns (33%), which are near the reported data for the bulk crystals (15).

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brid perovskites and introduces a new family of 2D solution-processed semiconductors for nanoscale optoelectronic devices.

REFERENCES AND NOTES
21. Materials and methods are available as supplementary materials on Science Online.

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SUPPLEMENTARY MATERIALS
www.sciencemag.org/content/349/6255/1518/suppl/DC1
Materials and Methods
Supplementary Text
Figs. S1 to S17
Tables S1 to S4
References (34, 35)
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Fig. 3. PL properties of the 2D (C4H9NH3)2PbBr4 sheets. (A) Steady-state PL spectrum of a piece of bulk crystal and several 2D sheets. (B) The corresponding optical image of the bulk crystal under excitation. Scale bar, 20 μm. (C to E) Optical images of the 2D sheets with 22 layers, 8 layers, and 3 layers. Scale bars, 2 μm. (F) SEM image of a 2D sheet. Scale bar, 2 μm. (G) The corresponding cathodoluminescence image showing the emission (with a 40-nm bandpass filter centered at 415 nm). (H) PL spectra of a 2D sheet at 298 and 6 K. (I) Time-resolved PL measurements showing a bi-exponential decay.

Fig. 4. Photoluminescence of different 2D hybrid perovskites. (C4H9NH3)2PbCl4 (i), (C4H9NH3)2PbBr4 (ii), (C6H13NH3)2PbCl4 (iii), (C6H13NH3)2PbBr4 (iv), (C4H9NH3)2PbBr2 (v), and (C4H9NH3)2CH3NH3PbBr2 (vi). 2D sheets demonstrate that the solution-phase direct growth method is generalizable. The corresponding optical PL images are shown in the inset. Scale bars, 2 μm for (i) to (v) and 10 μm for (vi).