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Atomically thin two-dimensional organic-inorganic hybrid perovskites.

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Organic-inorganic hybrid perovskites, which have proved to be promising semiconductor materials, exhibit an unusual structural relaxation, and this structural change leads to a band gap shape and large size. In contrast to other 2D materials, the hybrid perovskite sheets are made with halide. The variable of the organic chains (CH$_3$NH$_3$) with a structure similar to BaTiO$_3$. In the opposite case where the metal cation layers between the two layers, has probably delayed investigation of free-standing single layers of such 2D materials. Very recently, attempts to obtain ultrathin 2D perovskite single crystals 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 ([C$_4$H$_9$NH$_3$]$_2$PbBr$_4$) 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. In contrast to 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. In contrast to other 2D materials, a structural relaxation (or lattice constant expansion) occurred in the hybrid perovskite 2D sheets that could be responsible for emergent features.
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 (±0.2 nm) (Fig. 1, C and D). 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 (lattice constant a = 8.38 Å), 4.25 (lattice constant b = 8.50 Å), 5.81, 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 577 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
Pb-Br-Pb bond angle of 152.94° (see fig. S13 and tables S3 and S4 for more details), which may provide driving forces for lattice relaxation in the 2D thin sheet. In other reported 2D materials, the in-plane crystal structure does not change from the bulk crystal to isolated sheets; and the optical and electronic properties change because of electronic decoupling between adjacent layers.

We investigated the PL properties of individual 2D crystals under 325-nm laser excitation. Figure 3A shows the PL spectra of the bulk (C4H9NH3)2PbBr4 crystal and 2D sheets with different thickness (22, 8, and 3 layers thick, see fig. S14 for AFM images), and Fig. 3, B to E, shows the corresponding PL image of each sheet. Both the bulk materials and the sheets exhibit similar strong purple-light emission. The bulk crystal has an emission peak at 411 nm (2.97 eV), and the 2D sheets have slightly blue-shifted peaks at ~406 nm (3.01 eV). The slightly increased optical band gap for the ultrathin 2D sheets is probably induced by the lattice expansion. Our DFT simulation also suggests a 20-meV blue shift in PL for the single-layer 2D sheets, which is a trend consistent with the experimental observation. The 2D sheets with different thickness (from 22 to 3 layers) have similar PL spectra, the peak position shift is within 1 nm, and any lattice constant difference is within the experimental error from SAED observed between these samples. More discussion about the PL can be found in the supplementary text.

Cathodoluminescence microscopy, a technique that provides a map of the light emitted from a sample when excited by a focused electron beam 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 $\Gamma_1$ state, which cannot be distinguished from the $\Gamma_2$ 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). The chemistry of synthesizing these ultrathin 2D sheets was extended to other hybrid perovskites. We prepared (C4H9NH3)2PbCl4, (C4H9NH3)2PbI4, (C4H9NH3)2PbCl3Br, (C4H9NH3)3PbBr3I2, and (C4H9NH3)(CH3NH3)Pb2Br7 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)2PbCl4 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)3PbI4 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 crystal, (C4H9NH3)2PbClBr4 (iv), the band edge emission peak was at 385 nm, and a broad self-trapped exciton emission appeared at longer wavelength. However, the bromide-iodide alloy (v) showed only one peak at 505 nm. In the case of (C4H9NH3)3(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, 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 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...
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. (C6H5NH3)2PbCl4 (i), (C6H5NH3)2PbBr4 (ii), (C6H5NH3)2PbI4 (iii), (C6H5NH3)2PbCl2Br2 (iv), (C6H5NH3)2PbBr2I2 (v), and (C6H5NH3)2(CH3NH3)Pb2Br7 (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).

hybrid perovskites is flexible and deformable; and unlike the bulk crystal, the thin 2D sheets exhibit new features such as structural relaxation and PL shift. This study opens up opportunities for fundamental research on the synthesis and characterization of atomically thin 2D hybrid 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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