Two-Dimensional CH$_3$NH$_3$PbI$_3$ Perovskite: Synthesis and Optoelectronic Application

Jingying Liu,†‡ Yunzhou Xue,†‡ Ziyu Wang,†‡ Zai-Quan Xu,† Changxi Zheng,§ Bent Weber,⊥ Jingchao Song,‡ Yusheg Wang,‡ Yueerui Lu,¶ Yupeng Zhang,†§ and Qiaoliang Bao,†‡§

†Department of Materials Science and Engineering, §Department of Civil Engineering, and †School of Physics, Monash University, Wellington Road, Clayton, Victoria 3800, Australia
‡Institute of Functional Nano and Soft Materials (FUNSOM), Jiangsu Key Laboratory for Carbon-Based Functional Materials and Devices, and Collaborative Innovation Center of Suzhou Nano Science and Technology, Soochow University, Suzhou 215123, People’s Republic of China
⊥Research School of Engineering, College of Engineering and Computer Science, the Australian National University, Canberra, ACT 2601, Australia

Supporting Information

ABSTRACT: Hybrid organic—inorganic perovskite materials have received substantial research attention due to their impressively high performance in photovoltaic devices. As one of the oldest functional materials, it is intriguing to explore the optoelectronic properties in perovskite after reducing it into a few atomic layers in which two-dimensional (2D) confinement may get involved. In this work, we report a combined solution process and vapor-phase conversion method to synthesize 2D hybrid organic—inorganic perovskite (i.e., CH$_3$NH$_3$PbI$_3$) nanocrystals as thin as a single unit cell (~1.3 nm). High-quality 2D perovskite crystals have triangle and hexagonal shapes, exhibiting tunable photoluminescence while the thickness or composition is changed. Due to the high quantum efficiency and excellent photoelectric properties in 2D perovskites, a high-performance photodetector was demonstrated, in which the current can be enhanced significantly by shining 405 and 532 nm lasers, showing photoresponsivities of 22 and 12 A W$^{-1}$ with a voltage bias of 1 V, respectively. The excellent optoelectronic properties make 2D perovskites building blocks to construct 2D heterostructures for wider optoelectronic applications.

KEYWORDS: two-dimensional material, hybrid organic—inorganic perovskite, optoelectronic, photodetector

The rapid progress in graphene$^1$ and the methodology developed in preparing ultrathin atomic layer materials$^2$ has led to exploration of other two-dimensional (2D) materials such as hexagonal boron nitride (h-BN),$^3$ transition metal dichalcogenides (TMDs),$^4$−$^6$ and black phosphorus,$^7$−$^9$ etc. In particular, 2D semiconductor materials have received significant attention due to strong quantum confinement and the sizable band gap in these materials, which are desired for many optoelectronic applications. Recently, hybrid organic—inorganic perovskites described by the formula ABX$_3$ (A = CH$_3$NH$_3^+$; B = Pb$^{2+}$ or Sn$^{2+}$; and X = Cl$^-$, I$^-$, and/or Br$^-$) have been intensively studied as an emerging material for solar energy harvesting due to impressive power conversion efficiency over 20%.$^{10}$−$^{12}$ These materials have many interesting properties such as intrinsic ambipolar transport, high optical absorption coefficient in visible spectral range, changeable band gap, high quantum efficiency, and a long carrier diffusion length,$^{13,14}$ showing promising potential for optoelectronic and photonic devices such as solar cells,$^{15,16}$ photodetectors,$^{17}$ light-emitting diodes,$^{18}$ field-effect transistors,$^{19}$ waveguides,$^{20}$ as well as nanolasers.$^{21}$ It is intriguing to investigate the optoelectronic properties in 2D perovskite after reducing it into single- and few-unit-cell-thick crystals in which 2D quantum wells are exposed and the electronic coupling between the top and bottom layers may be varied.

A variety of methods have been developed to synthesize the perovskite from polycrystalline film to bulk single crystal.$^{14}$ However, the introduction of many defects and grain boundaries in three-dimensional (3D) bulk perovskite is unavoidable,$^{22}$ which could degrade the optoelectronic properties. Niu et al.$^{23}$ successfully produced ultrathin 2D perovskite flakes using micromechanical exfoliation as used for graphene and found distinct exciton properties in thick and thin regions. Xiong and co-workers$^{24,25}$ reported the synthesis of perovskite...
nanoplatelets with a thickness from dozens to several hundred nanometers by using the chemical vapor deposition (CVD) method, bringing us a step closer to produce ultrathin perovskite. Liao et al.\textsuperscript{26} reported a one-step solution self-assembly method to prepare a single-crystalline square microdisk of CH$_3$NH$_3$PbI$_3$ with a thickness of about 500 nm. However, how to synthesize ultrathin 2D perovskite with a thickness down to a single unit cell is still challenging because of the poor chemical stability, fast crystallization rate, and the intrinsically non-van der Waals-type 3D characteristics of perovskite. The uncontrolled growth of perovskite will produce grains with random crystal size and large morphological variations, leading to very different photovoltaic performance in the resulting devices, which represents one of the major barriers for practical applications.\textsuperscript{27} In this regard, the realization of 2D perovskite with several unit cells (less than 10 nm), even with single-unit-cell thickness, will contribute to a comprehensive understanding of the intrinsic physical properties, especially charge carrier behaviors, which are the basis of perovskite-based functional optoelectronic devices. Very recently, Dou and co-workers\textsuperscript{28} reported the solution-phase growth of single- and few-unit-cell-thick 2D hybrid perovskites of (C$_4$H$_9$NH$_3$)$_2$PbBr$_4$ with well-defined square shape and large size. They also found that the color tuning of the photoluminescence (PL) spectrum could be achieved by changing the sheet thickness as well as composition. However, the one-step solution process limits the composition modification of (C$_4$H$_9$NH$_3$)$_2$PbBr$_4$ perovskite somewhat, making it difficult to obtain 2D CH$_3$NH$_3$PbX$_3$ (X = Cl$^-$, Br$^-$, or I$^-$) perovskites, which have better photovoltaic performance and a broader range of applications.\textsuperscript{29} Synthesis and device application of 2D CH$_3$NH$_3$PbX$_3$ perovskite are thus of strategic interest.

In this work, we demonstrate the preparation of 2D CH$_3$NH$_3$PbX$_3$ perovskites as thin as a single unit cell, using a combined solution process and vapor-phase conversion method. In particular, the 2D PbI$_2$ was used as the template, resulting in the growth of a non-van der Waals-type 2D perovskite (i.e., CH$_3$NH$_3$PbI$_3$). This two-step process is highly versatile to produce many different 2D perovskites pertaining to the same structural framework through the intercalation of different organic cations or halogen anions. Owing to the character of single- or few-unit-cell thickness, it is interesting to

![Figure 1](https://example.com/figure1.png)

**Figure 1.** (a) Schematic illustration of solution process to fabricate 2D PbI$_2$ nanosheets and vapor-phase conversion process to transfer PbI$_2$ into 2D CH$_3$NH$_3$PbI$_3$ perovskite nanosheets. (b) Crystal structure of single-unit-cell-thick 2D CH$_3$NH$_3$PbI$_3$ perovskite. (c) Optical image of 2D CH$_3$NH$_3$PbI$_3$ nanosheets synthesized by hot casting (>90 °C) and vapor-phase conversion. Scale bar: 10 μm. (d) High-magnification optical image of 2D CH$_3$NH$_3$PbI$_3$ nanosheets. Scale bar: 4 μm. (e) PL mapping image of 2D CH$_3$NH$_3$PbI$_3$ nanosheets shown in (d). Scale bar: 4 μm. (f) Optical image of 2D CH$_3$NH$_3$PbI$_3$ nanosheets synthesized by hot casting (<90 °C) and vapor-phase conversion. Scale bar: 10 μm. (g) High-magnification optical image of 2D CH$_3$NH$_3$PbI$_3$ nanosheets. Scale bar: 4 μm. (h) PL mapping image of 2D CH$_3$NH$_3$PbI$_3$ nanosheets shown in (g). Scale bar: 4 μm. (i) XRD patterns of PbI$_2$ nanosheets and converted CH$_3$NH$_3$PbI$_3$ nanosheets. (j) Low-magnification TEM image of a 2D CH$_3$NH$_3$PbI$_3$ nanosheet. Scale bar: 0.5 μm. The inset shows an electron diffraction pattern of the nanosheet. (k) High-resolution TEM image of a 2D CH$_3$NH$_3$PbI$_3$ nanosheet. Scale bar: 2 nm.
CH3NH3PbI3. The height profile indicates a thickness of 1.3 nm. (b) Two-layer CH3NH3PbI3. The height profile indicates a thickness of 2.5 nm. (c) Four-layer CH3NH3PbI3. The height profile indicates a thickness of 5.0 nm. (d) Ten-layer CH3NH3PbI3. The height profile indicates a thickness of 13.0 nm. (e) Normalized PL spectra of 2D perovskite nanosheets with different thicknesses. (f) PL peak position and energy gap as a function of the number of unit cells in perovskite.

Figure 2. (a–d) AFM topography images of 2D CH3NH3PbI3 nanosheets with different thicknesses. Scale bars: 2 μm. (a) Single-layer CH3NH3PbI3. The height profile indicates a thickness of 1.3 nm. (b) Two-layer CH3NH3PbI3. The height profile indicates a thickness of 2.5 nm. (c) Four-layer CH3NH3PbI3. The height profile indicates a thickness of 5.0 nm. (d) Ten-layer CH3NH3PbI3. The height profile indicates a thickness of 13.0 nm. (e) Normalized PL spectra of 2D perovskite nanosheets with different thicknesses. (f) PL peak position and energy gap as a function of the number of unit cells in perovskite.

find that the 2D perovskite exhibits high PL quantum yield, unique band structure compared to the bulk crystal, and excellent photodetection performance.

RESULTS AND DISCUSSION

The 2D hybrid organic–inorganic perovskite nanosheets were prepared by a two-step method, as schematically shown in Figure 1a. This method involves casting saturated PbI2 aqueous solution onto a substrate and subsequently heating the substrate at an elevated temperature, during which 2D PbI2 nanosheets will nucleate. Subsequently, the 2D CH3NH3PbI3 perovskite nanosheets were formed by intercalating the CH3NH3I molecules into the interval sites of PbI6 octahedron layers. The resulting CH3NH3PbI3 perovskite still maintains the 2D lamellar structure, indicating good morphology retention after vapor-phase conversion. It is found that the heating temperature in the solution process is crucial to affect the nucleation and growth of 2D PbI2 nanosheets because the number of nucleation sites is controlled by temperature. When the temperature is greater than 90 °C, the crystal growth rate is much higher than the nucleation rate, and a large amount of thick PbI2 crystals will precipitate on the substrate. Nevertheless, some triangular or hexagonal 2D PbI2 nanosheets with single-crystalline nature can still be observed at a particular region on the substrate (Figure 1c,d) upon the concentration change of PbI2 solution during drying in about 100 s. The 2D structure indicates that the out-of-plane growth rate along the c-axis is much lower than that of the in-plane one. This is because of different surface energies along different directions; that is, generally lower surface energy is expected along the in-plane direction and thus leads to a faster growth rate. Due to the high-temperature growth process, the crystal quality is high, resulting in high PL quantum yield after converting PbI2 into CH3NH3PbI3. The high and uniform PL intensity over the whole CH3NH3PbI3 crystal (Figure 1e) suggests that the sample maintains good uniformity and continuity after the conversion process. By contrast, low temperature (<90 °C) in the hot casting process could increase the quantity of the crystal nucleus and inhibit the crystal growth rate to achieve large-scale production of 2D PbI2 nanosheets (Figure 1f,g). However, the low-temperature growth process always lasts for 30 min to 1 h. It should be noted that the PbI2 is also unstable in H2O. During the slow growth process at low temperature, there is a competitive relationship between the PbI2 crystal growth and redissolution, which will affect the crystal quality inevitably, leading to relatively low PL intensity (Figure 1h) in resulting CH3NH3PbI3 nanosheets. The corresponding AFM image (Supporting Information, Figure S1) of a perovskite nanosheet reveals jagged edges, which is evidence of redissolution. Compared with CVD methods, the solution process can produce PbI2 crystals with well-controlled morphologies. The PbI2 and subsequent CH3NH3PbI3 nanowires, nanobelts, and nanosheets with different diameters and thicknesses can be obtained by controlling the evaporation rate of solvent, which is associated with solvent type and the temperature of solvent and substrate (see Figure S2 in Supporting Information).

X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used to investigate the microstructure of PbI2 and CH3NH3PbI3 nanosheets. Figure 1i shows the XRD results of PbI2 and CH3NH3PbI3 nanosheets grown on glass substrates. The XRD pattern of PbI2 shows four dominant diffraction peaks at 12.8, 25.6, 38.5, and 52.3°, which can be assigned to the (001), (002), (003), and (004) facets, respectively, of the 2H hexagonal crystalline structure. After the CVD conversion process, two new peaks at 14.1 and 28.5° are observed, which can be indexed to (110) and (220) facets, respectively, of the tetragonal structure of perovskite. It should be noted that the diffraction peaks of PbI2 disappeared, suggesting a complete conversion of PbI2 into perovskite crystals. More interestingly, a few XRD peaks such as (112), (211), (310), and (224), which normally appear in solution-
that the surface of 2D CH$_3$NH$_3$PbI$_3$ nanosheets becomes skite nanosheets with different numbers of layers were investigated by AFM, as shown in Figure 2a–d. It is found that the surface of 2D CH$_3$NH$_3$PbI$_3$ nanosheets becomes relatively rough compared to that of the PbI$_2$ nanosheets, due to the adsorption of CH$_3$NH$_3$I molecules on the surfaces. AFM topography indicates a surface roughness of 0.2−1.0 nm. The height profiles depict perovskite thicknesses of 1.3, 2.5, 5.0, and 13 nm, corresponding to 1, 2, 4, and 10 unit cells, respectively. The thickness of single-unit-cell CH$_3$NH$_3$PbI$_3$ is smaller than that of single-unit-cell (C$_4$H$_9$NH$_3$)$_2$PbBr$_4$ because of the smaller radius of the CH$_3$NH$_3^{+}$ ion. To the best of our knowledge, this is the first report on the synthesis of CH$_3$NH$_3$PbX$_3$ perovskite with 2D structure, which may show unique optical and electrical properties.

In order to investigate the optical properties of 2D perovskite nanosheets with different thicknesses, PL spectroscopy measurements were implemented under 532 nm laser excitation, as shown in Figure 2e,f. Both bulk crystals and 2D sheets with different thicknesses exhibit high quantum efficiency in terms of PL yield. However, the PL peaks shift to shorter wavelength gradually when decreasing the perovskite thickness. For the perovskite with single-unit-cell thickness, the PL peak is located around 720 nm. As reported by Dou et al., the shift of PL emission for the ultrathin 2D perovskite sheets is probably induced by the lattice expansion; that is, the structural relaxation of the in-plane crystal lattice could increase the optical band gap. It is interesting to find that the change of band gap in 2D CH$_3$NH$_3$PbI$_3$ is more pronounced than that of 2D (C$_4$H$_9$NH$_3$)$_2$PbBr$_4$ reported in ref 28. Generally, the electronic structure of hybrid organic−inorganic perovskite compounds (ABX$_3$) is governed by the B−X bond of the inorganic framework. Although A cation does not directly affect the electrical structure, a large A cation can cause distortion of the B−X bonds, thus adversely affecting symmetry. While smaller A cations are intercalated into the interval sites of PbI$_6$ octahedrons layers, the B−X bonds undergo compression and the A−X bonds undergo tension to compensate for the excess space. Conversely, in the case of larger A cations, a higher degree of symmetry will be induced, resulting in a more stable electrical structure. As a result, a broader tuning wavelength could be achieved for 2D CH$_3$NH$_3$PbX$_3$ because the radius of the CH$_3$NH$_3^{+}$ ion is much smaller than that of (C$_4$H$_9$NH$_3$)$_2^{+}$. Furthermore, there is no PL peak position shift between these crystals with different shapes (Supporting Information, Figure S7).
The photocurrent to increase to 70% of the ON-state current. The fall time (<40 ms) is dependent on the applied bias, indicating ohmic contact between perovskite and gold electrodes. The ratio of current at different power are shown in Figure 4 c. Clearly, the photocurrent to dark current can reach up to 2 orders of magnitude at different power (<10 pw), close to nonconductive, 2 orders of magnitude at different power (<10 pw), close to nonconductive.) Figure 4d reveals distinct PL emission from CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$PbBr$_3$, where CH$_3$NH$_3$PbI$_3$ (inner triangle) and CH$_3$NH$_3$PbBr$_3$ (surrounding region) are laterally connected with well-defined interface.

We further fabricate a field-effect transistor to evaluate the electronic and photoelectric properties of a 2D CH$_3$NH$_3$PbI$_3$ sheet. The perovskite-based transistor device with a back gate is schematically shown in Figure 4a. In order to prevent doping by contamination, a lithography-free technique with electrode materials with a patterned Si$_x$N$_y$ shadow mask was used to fabricate clean devices. Figure 4b shows the optical and PL mapping images of the transistor device based on single-unit-cell perovskite. It is notable that the source–drain current ($I_{DS}$) is very small (about 10$^{-12}$ A, close to nonconductive) in dark conditions, and the $I_{DS}$ could not be tuned by gate voltage, which is very different from the bulk materials. However, even under the illumination of a dim light, the current of the 2D perovskite-based device could be significantly enhanced, promising great potential as an effective photodetector. Typical $I$–$V$ curves of the 2D perovskite-based device under the irradiation of natural light with different power are shown in Figure 4c. Clearly, $I$–$V$ curves present linear dependence on the applied bias, indicating ohmic contact between perovskite and gold electrodes. The ratio of photocurrent to dark current can reach up to 2 orders of magnitude (Figure 4c, inset), which is attributed to strong light–matter interaction as well as broad-band light-harvesting capability in a single-unit-cell perovskite nanosheet. However, when the 2D perovskite-based device was illuminated by a weak laser (405 or 532 nm, unfocused, the effective power <10 pw), the hysteresis can be observed in $I$–$V$ curves; that is, the...
current depends on the direction of the voltage sweeping between the source and drain electrodes (Supporting Information, Figure S9). It is supposed to be related to the poling effect in CH₃NH₃PbI₃. Nevertheless, the 2D perovskite-based photodetector is sensitive to a broad-band light from the ultraviolet to the entire visible spectral range. Time-dependent photocurrent was measured under the illumination of natural light (inset of Figure 4c), a 405 nm laser (Figure 4d), and a 532 nm laser (Supporting Information, Figure S10), indicating effective optical switching. The photoresponsivities of the phototransistor with a voltage bias of 1 V were calculated to be 22 AW⁻¹ under a 405 nm laser and 12 AW⁻¹ under a 532 nm laser. These are much higher than that of photodetectors based on bulk perovskite film (3 AW⁻¹) but slightly lower than perovskite microplate crystals (40 AW⁻¹). As one of the key figures of merit, the relatively faster response time can also naturally broaden the scope of the device application. It is found that the rise and decay times of the photodetector based on 2D CH₃NH₃PbI₃ nanosheets are shorter than 20 and 40 ms, respectively (Figure 4f), suggesting a much faster response time than photodetectors based on bulk films. The results above show that the 2D perovskite device has excellent photoresponsivity and relatively fast response time for light detection, which affords the potential for application in optoelectronic switches and photodetectors.

CONCLUSION

In summary, we have successfully demonstrated a facile method to produce atomically thin 2D CH₃NH₃PbX₃ (X = Cl, Br, or I) perovskite nanosheets and heterostructure. The high-quality 2D perovskite crystals exhibit high PL quantum efficiency with broad wavelength tunability. The excellent optical and photoelectric properties make 2D perovskite a promising candidate for high-performance photodetectors. The realization of 2D perovskite with several-unit-cell (less than 10 nm) and even single-unit-cell thickness can open up exciting opportunities for the fundamental understanding of this type of materials and creation of a wide range of functional devices, ranging from photovoltaics and photodetectors to light-emitting diodes and laser diodes.

METHODS

The 2D CH₃NH₃PbI₃ perovskite nanosheets were prepared by two steps. First, saturated PbI₂ aqueous solution was prepared by dissolving 1 mg of PbI₂ powder (Sigma-Aldrich) in 1 mL of DI water and heated at 90 °C for 1 h. Then the solution was drop-casted on the SiO₂/Si substrate and heated at a temperature from 30 to 180 °C. The 2D PbI₂ nanosheets nucleate on the substrate during drying. In the second step, the CH₃NH₃I powder, which was synthesized according to previous work, was placed at the center of a CVD furnace while the as-grown 2D PbI₂ nanosheets on the silicon oxide substrate were mounted downstream of the apparatus. The central heating zone was increased to 120 °C under low-pressure conditions (40–50 Torr) and maintained for 40 min to 4 h. Ar and H₂ were introduced into the quartz tube as carrier gases with flow rates of 35 and 15 sccm, respectively, during the whole vapor conversion process. The furnace was then naturally cooled to room temperature with the cover closed at a cooling rate of 5 °C/min. The 2D CH₃NH₃PbBr₃, CH₃NH₃PbI₃, and CH₃NH₃PbBrI₃ nanosheets were synthesized by controllably annealing as-grown CH₃NH₃PbI₃ nanosheets in an excess CH₃NH₃Br vapor environment at 120 °C under low pressure (40–50 Torr) with different holding times (from 15 min to 2 h). Different annealing times result in complete or partial halogen element substitution.

The morphologies and topography of the 2D CH₃NH₃PbI₃ perovskite nanosheets were characterized using optical microscopy and atomic force microscopy (Bruker, Dimension Icon SPM). XRD experiments were conducted by a Philips X-ray diffractometer with Cu Kα radiation. The samples were scanned from 10 to 60° with a step size of 0.02°. The microstructure of the samples and electron diffraction pattern were characterized using a TEM microscope (FEI, Tecnai G2 F20). PL measurements were performed using a confocal microscope system (WITEC, alpha 300R) with a 100× objective lens (NA = 0.9) in ambient conditions. We used 450 and 532 nm lasers to excite samples, which were placed on a piezo-crystal-controlled scanning stage. The spectra are collected using 600 lines/mm gratings with a spectral resolution of <0.09 nm. To avoid sample damage, low laser power (5 μW) was applied during the measurements. The exposure time was 0.01 s, and the accumulation number was 10. Many different locations of the sample were tested, and an average was made to conclude the PL peak position of each sample.

The 2D CH₃NH₃PbI₃-based phototransistor devices were fabricated on a SiO₂/Si substrate. The electrodes were patterned using parallel SiN₄ grids as a shadow mask to define the deposition region, followed by electron beam deposition of Ti/Au (5/50 nm) in vacuum with a chamber pressure of <6 × 10⁻⁶ Torr. The channel length between the source and drain electrodes was around 10 μm. The source–drain current as a function of bias voltage upon an unfocused 405 nm laser, a 532 nm laser, and natural light illumination was recorded by a source meter unit (Agilent, B2902A).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.5b07791.

Additional figures and experimental details (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: yupeng.zhang@monash.edu.
*E-mail: qlbao@suda.edu.cn.

Author Contributions

J.L., Y.X., and Z.W. contributed equally to this work.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by ARC DECRA (DE120101569) and DSI top-up grant, DP (DPI140101501), Engineering Seed Fund in Monash University, J.L. and Z.W. acknowledge support from the MCATM scholarship at Monash University. Q.B. also acknowledges the support from 863 Program (Grant No. 2013AA031903), the youth 973 program (2015CB932700), the National Natural Science Foundation of China (Grant Nos. 10222208, 101290273, 91433107), China Postdoctoral Science Foundation (2014M550303), the Priority Academic Program Development of Jiangsu Higher Education Institutions, and Collaborative Innovation Center of Suzhou Nano Science and Technology. This work was performed in part at the Melbourne Centre for Nanofabrication (MCN) in the Victorian Node of the Australian National Fabrication Facility (ANFF).

REFERENCES


Two-Dimensional CH$_3$NH$_3$PbI$_3$ Perovskite: Synthesis and Optoelectronic Application

Jingying Liu$^{†,||}$, Yunzhou Xue$^{‡,||}$, Ziyu Wang$^{‡,||}$, Zai-Quan Xu$^†$, Changxi Zheng$^§$, Bent Weber$^⊥$, Jingchao Song$^†$, Yusheng Wang$^‡$, Yuerui Lu$^*$, Yupeng Zhang$^*,†$, and Qiaoliang Bao$^*,‡,†$

$^†$Department of Materials Science and Engineering, Monash University, Wellington Road, Clayton, Victoria 3800, Australia.

$‡$Institute of Functional Nano and Soft Materials (FUNSOM), Jiangsu Key Laboratory for Carbon-Based Functional Materials and Devices, and Collaborative Innovation Center of Suzhou Nano Science and Technology, Soochow University, Suzhou 215123, P. R. China.

$§$Department of Civil Engineering, Monash University, Clayton 3800, Victoria, Australia.

$⊥$School of Physics, Monash University, Monash 3800, Victoria, Australia.

$*$College of Engineering and Computer Science, Australian National University, Australia

$||$These authors contributed equally to this work.

*Address correspondence to qlbao@suda.edu.cn (Q. Bao), yupeng.zhang@monash.edu (Y. Zhang)

**KEYWORDS**: two-dimensional material, hybrid organic-inorganic perovskite, optoelectronics, photodetector
Figure S1. AFM topography image of 2D perovskite nanosheet produced by a combined low temperature solution process and CVD method. Scale bar: 2 µm.

The low temperature growth process always lasts for 30 mins to 1 hour. An important issue should to be noted is that the PbI$_2$ is also unstable in H$_2$O. During the slow growth process with low temperature, there is a competitive relationship between the PbI$_2$ crystal growth and re-dissolution, which will affect the crystal quality inevitably. The corresponding AFM image (Figure S1) for perovskite nanosheets reveals the re-dissolution clearly during the solution process, that is, the crystal exhibited the jagged edges.
Compared with CVD method to synthesize the PbI₂ crystals, the morphology of PbI₂ crystals could be more controlled by our solution process. The PbI₂ and subsequent CH₃NH₃PbI₃ nanowires, nanobelts, and microsheets with different diameters and thicknesses could be obtained, as shown in Figure S2.

PbI₂ microsheets: Owing to the different solubility of PbI₂ in water at different temperatures, we developed a new crystallization method to prepare PbI₂ microsheets.
By inversing the growth temperature, the resulting PbI$_2$ microsheets with different diameters and thicknesses could be produced (Figure S2a-d).

PbI$_2$ nanowires: When dissolving 0.5g PbI$_2$ powder in N,N-dimethylmethanamide (DMF) solution at 90 °C for 1 hour, followed by the 12 hours standing time with deionized water added into the PbI$_2$/DMF solution, the PbI$_2$ nanowires will precipitate out (Figure S2e-h).

PbBr$_2$ nanobelts: Owing to the different solubility of PbBr$_2$ in water at different temperatures, by inversing the growth temperature, the resulting PbBr$_2$ nanobelts with different diameters and thicknesses could be produced (Figure S2i-l).

Similarly, the CH$_3$NH$_3$PbI$_3$ perovskites in different morphology can be formed through intercalating the CH$_3$NH$_3$I molecules into the interval sites of PbI$_6$ octahedrons layers by using CVD method.
XRD patterns are obtained from different samples produced by CVD process (2D nanosheets) and conventional spin-coating (polycrystalline thin film). The XRD patterns of perovskite nanosheets does not reveal the presence of other orientations: (112), (211), (310), and (224), indicating that the 2D CH$_3$NH$_3$PbI$_3$ nanosheets obtained by our method are highly crystallized and have preferred orientation on substrate.
Figure S4 (a) Low magnification TEM image of a 2D PbI₂ nanosheet. Scale bar: 2 µm. (b) Selected-area electron diffraction pattern of PbI₂ nanosheet along the [0001] zone axis. Scale bar: 2 Å/nm.

Figure S4a and b show the low magnification TEM image and the selected-area electron diffraction pattern taken from the as-grown PbI₂ nanosheet, indicating a highly crystalline PbI₂ with six-fold symmetric diffraction patterns.
Figure S5 Electron diffraction pattern of 2D perovskite nanosheet under high energy electron beam irradiation. Scale bar: 2 Å/nm.

It should be noted that the perovskite was sensitive to electron beam or laser irradiation, PbI$_2$ reflections are also evident in the diffraction patterns under the long irradiation time (Figure S5). This is due to localized loss of CH$_3$NH$_3$I under electron beam or laser irradiation, leaving small regions of PbI$_2$. The rewritable characteristic under electron beam or laser will make this type of perovskites promising candidates for fabricating novel functional devices, which needs further investigation.
Figure S6 The relaxed structures for the tetragonal phase perovskite with different MA⁺ intercalation ratios. (a) CH₃NH₃/Pb=0.25. (b) CH₃NH₃/Pb=1.

Table 1 The lattice constants of tetragonal perovskite (AyBX₃) with different intercalation ratios of CH₃NH₃.

<table>
<thead>
<tr>
<th>y</th>
<th>Lattice type</th>
<th>Lattice parameters, a, b and c in Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>Monoclinic</td>
<td>a=8.6613, b=8.9722, c=12.1651, α=90.00°, β=90.00°, γ=86.43°</td>
</tr>
<tr>
<td>0.5</td>
<td></td>
<td>a=9.2047, b=8.9159, c=12.3357, α=90.00°, β=90.00°, γ=86.53°</td>
</tr>
<tr>
<td>0.75</td>
<td></td>
<td>a=8.9251, b=8.9608, c=12.6323, α=90.02°, β=90.29°, γ=89.35°</td>
</tr>
<tr>
<td>1</td>
<td>Tetragonal</td>
<td>a=b=9.2419, c=12.8838, α=β=γ=90.00°</td>
</tr>
</tbody>
</table>

All the calculations were performed by Vienna Ab-initio Simulation Package (VASP). Project augment wave (PAW) method was used to describe the interaction between the ion and valence electrons. The exchange-correlation functional developed by Perdew, Burke and Ernzerhof (PBE) was used. The energy cutoff of all the calculations was set to 500 eV. A Monkhorst-pack k-point mesh with density of 4×4×2 was used in the calculations of tetragonal phase. The tetragonal phase of ABX₃ was modelled by a $\sqrt{2} \times \sqrt{2} \times 2$ supercell of the cubic unit cell with four CH₃NH₃.
molecules in it. To simulate the perovskite crystal structure with different CH$_3$NH$_3$ molecules, the corresponding numbers of CH$_3$NH$_3$ molecules were added from the simulation cell. In the initial structure, the C-N bond of all CH$_3$NH$_3$ molecules was set to align in the <100> direction of the cubic unit cell. Then all the structures were relaxed until the force exerted on each atom is less than 0.01 eV/Å$^2$.

The DFT calculations results (Figure S6) suggest that the crystal structure transforms from hexagonal to monoclinic system when the CH$_3$NH$_3$I molecules start to intercalate into the interval sites of PbI$_6$ octahedrons layers. However, due to the completely conversion of PbI$_2$ into CH$_3$NH$_3$PbI$_3$ perovskite, the length of c-axis could be increased and the shear stress in a-b plane will be introduced, which changes the $\gamma$ angle. As a result, the lattice changes from monoclinic to tetragonal structure.

Figure S7 (a) and (b) AFM topography images of 2D CH$_3$NH$_3$PbI$_3$ nanosheets with the same thickness but different shapes (a: Triangle; b: Hexagon). Scale bars: 2 µm. (c) PL spectra collected from a and b.

Figure S7 a and b show the AFM topography image of the truncated triangular and hexagonal nanosheets with the same thickness. The PL spectra in Figure S7c are collected from the sample in a and b. It can be seen that these is no clear PL peak shift between these two spectra, indicating the same phase and structure. The intensity
difference of the PL spectra might be due to the different laser intensities, focusing conditions or integration times.

Figure S8 Normalized PL spectra of 2D perovskite nanosheets with different compositions. Red trace: CH$_3$NH$_3$PbI$_3$; orange trace: CH$_3$NH$_3$PbBr$_x$I$_{3-x}$; green trace: CH$_3$NH$_3$PbBr$_3$. 

![Normalized PL intensity vs Wavelength (nm) graph]

The normalized PL intensity is plotted against the wavelength in nanometers (nm) for three different compositions: red trace represents CH$_3$NH$_3$PbI$_3$, orange trace represents CH$_3$NH$_3$PbBr$_x$I$_{3-x}$, and green trace represents CH$_3$NH$_3$PbBr$_3$. The peaks at different wavelengths indicate variations in the emitted light intensity due to the different compositions.
Figure S9 I-V curves of the 2D perovskite based device under the irradiation of weak unfocused 532 nm laser.

When the 2D perovskite based device was illuminated by weak laser (405 nm or 532 nm, unfocused, the effective power: <10 pw), the hysteresis can be observed in I-V curves, i.e. the current depends on the direction of the voltage sweeping between the source and drain electrodes. This means that some displacement (i.e. charge concentrations) related to the light intensity may happened, which could not be introduced by charge carriers injected from the contacts under forward bias.
Figure S10 (a) Time-dependent photocurrent measurement on perovskite phototransistor over a five-period on-off operation under the different illumination of 532 laser. (b) Temporal photocurrent response excited at 532 nm. The rise time (<25 ms) is defined as the time for the photocurrent increased to 70% of ON-state current. The fall time (<50 ms) is defined as the time for the photocurrent decreased by 70% of ON-state current. (c) Photocurrent and photoresponsivity versus optical illumination power at a wavelength of 532 nm with a voltage bias of 1V. (d) Photocurrent and photoresponsivity versus optical illumination power under natural light with a voltage bias of 1V.

Figure S10a shows the photocurrent response of the device under the irradiation of the 532 nm laser with different power. Compared with the photocurrent response under the irradiation of the 405 nm laser, it can be found that the higher photocurrent was generated under 405 nm laser, in agree with the higher absorbance at a shorter wavelength. Temporal photocurrent response of the transistor under 532 nm laser was measured, as shown in figure S9b. The result reveals that a rise time less than 25 ms and a fall time less than 50 ms (70%), which can be applicable for many applications.
Figure S10c and d shows the dependence of photocurrent and photoresponsivity on 532nm laser (c) and natural light (d) with a voltage bias of 1V. The photocurrent is increased linearly with promoting the light power. It can be seen that higher photoresponsivity can be achieved when decreasing the illumination power.

Figure S11. Optical images of larger size single crystal perovskite 2D nanosheets. Scale bars: 20 µm.