Recent progress of two-dimensional lead halide perovskite single crystals: Crystal growth, physical properties, and device applications

Jiayu Di | Jingjing Chang | Shengzhong (Frank) Liu

1State Key Discipline Laboratory of Wide Band Gap Semiconductor Technology, Shaanxi Joint Key Laboratory of Graphene, Advanced Interdisciplinary Research Center for Flexible Electronics, School of Microelectronics, Xidian University, Xi'an, China
2Key Laboratory of Applied Surface and Colloid Chemistry, Ministry of Education, Shaanxi Key Laboratory for Advanced Energy Devices, Shaanxi Engineering Lab for Advanced Energy Technology, Institute for Advanced Energy Materials, School of Materials Science and Engineering, Shaanxi Normal University, Xi'an, China
3Dalian National Laboratory for Clean Energy, iChEM, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, University of the Chinese Academy of Sciences, Chinese Academy of Sciences, Dalian, China

Correspondence
Jingjing Chang, State Key Discipline Laboratory of Wide Band Gap Semiconductor Technology, Shaanxi Joint Key Laboratory of Graphene, Advanced Interdisciplinary Research Center for Flexible Electronics, School of Microelectronics, Xidian University, 2 South Taibai Road, Xi'an 710071, China.
Shengzhong (Frank) Liu, Key Laboratory of Applied Surface and Colloid Chemistry, Ministry of Education, Shaanxi Key Laboratory for Advanced Energy Devices, Shaanxi Engineering Lab for Advanced Energy Technology, Institute for Advanced Energy Materials, School of Materials Science and Engineering, Shaanxi Normal University, Xi'an 710119, China.
Email: jjingchang@xidian.edu.cn (J. C.) and szliu@dicp.ac.cn (S.(F.)L.)

Abstract
In recent years, research on organic-inorganic lead halide two-dimensional (2D) perovskites has been blossoming. 2D perovskites have completely different layered structures from three-dimensional perovskites, with interleaved organic and inorganic layers, leading to 2D perovskite materials being more stable and possessing anisotropic electrical transport. Meanwhile, 2D organic-inorganic lead halide perovskite single crystals are receiving increasing attention because of their remarkable properties, such as long charge carrier lifetime, low defect density, and high photoluminescence quantum yield, increasing their potential for optoelectronic applications. Previously, a series of material systems based 2D perovskites single crystals has been synthesized and applied in various device applications. In this review, the preparation methods of organic-inorganic lead halide 2D perovskite single crystals, the growth principles, their photoelectric properties and several device applications are discussed.

KEYWORDS
2D perovskite, device applications, growth principles, single crystals

1 | INTRODUCTION
Energy is vital to human life, and solar energy is the best gift from above. Organic-inorganic lead halide perovskite has replaced the dye layer of dye-sensitized solar cells to become a new light-absorbing layer of solar cells, achieving high energy conversion efficiency (the current certified efficiency is as high as 25.2%), which stimulates...
promising research on the photoelectric properties of perovskite materials. Perovskite materials are not only used in perovskite solar cells (PSCs), but also in light-emitting diodes (LEDs), photodetectors, and so forth.

Perovskite material was discovered by Gustav Rose in 1839 and named after the Russian mineralogist Lev Perovski. “Perovskites” does not refer specifically to the complex oxides of calcium and titanium (CaTiO3), but rather to a series of compounds with the chemical formula ABX3. For the organic-inorganic halide perovskite, A in ABX3 is usually an organic group, such as CH7N2+(FA) or CH3NH3+(MA), B is a metal cation, like Pb2+ or Sn2+, and X is a halide anion, such as Cl-, Br-, or I-.

Compared to the structure of three-dimensional (3D) perovskite, the chemical formula of two-dimensional (2D) homologous perovskite is (A0)nAm−1BnX3n+1, where A0 is a monovalent (m = 2) or divalent (m = 1) long-chain organic cation, and the elements represented by A, B, X are the same as those of 3D perovskite. The relationship between 2D and 3D perovskites contains two aspects:

1. In 3D perovskite, octahedral BX64− is connected in a corner-sharing way and forms the cage in which the small organic group A is locked. The tolerance factor (TF) can be used to reflect the stability and distortion of the 3D perovskite crystal structure, and the octahedral factor (OF) is used to determine whether the B site has the right size to fit the X6 octahedron, and it is also an important factor in evaluating the structural stability. According to:

\[
TF = \frac{r_A + r_X}{\sqrt{2(r_B + r_X)}}
\]

\[
OF = \frac{r_B}{r_X}
\]

2. From the point of view of the formula, when n is equal to 1, the formula becomes A0mBX4. When n equals 2, the bread on each side changes from a corner-sharing octahedron to a single layer of perovskite. When n equals 3 or 4, the number of perovskite layers on each side is respectively 2, 3, and so forth (when n is not equal to 1 or infinity, it is called quasi-2D perovskite); as n approaches infinity, by ignoring the layer of the large organic group on the edge of the structure, the formula is (ABX3)n, with a common 3D perovskite single crystal lattice structure. Note that organic and inorganic layers are stacked in turn to form a graphene-like layered structure, and the interlayer interaction is via van der Waals forces.

The 2D perovskite is a very large material system. According to octahedral connection mode, it can be divided into three types: (100)-oriented, (010)-oriented and (001)-oriented 2D perovskites. The (110)-oriented material requires small, highly symmetric A’ cation to maintain structural stability. (111)-oriented material is a class of defective 2D perovskite lacking metal cations (B sites). The (100)-oriented 2D perovskite is widely studied at present and can be divided into three types (determined by the cation at the

---

**Figure 1** (PEA)2(MA)n−1PbnI3n+1 perovskite as an example. A, Schematic diagram of the unit cell structures for different n values, which shows the evolution of dimensionality from 2D (n = 1) to 3D (n = ∞). B, DFT simulation of the formation energy of perovskites with different n values in different atmospheres.

Source: Reproduced with permission: Copyright 2016, American Chemical Society
A site): the Ruddlesden-Popper (RP) phases, the Dion-Jacobson (DJ) phases, and the alternating cation in the interlayer space (ACI) type.

(a) RP phases. The octahedral element between layers is offset by (1/2, 1/2), like (BA)$_2$(MA)$_2$Pb$_3$I$_{10}$. (b) DJ phases. In DJ phase (3AMP)(MA)$_2$Pb$_3$I$_{10}$, the octahedrons do not show any shift (0, 0), but are perfectly stacked. (c) ACI type. The octahedron shows the displacement of (1/2, 0).

In addition to conventional 2D perovskite materials, the lead-free double perovskite, like typical symmetrical face-centered cubic Cs$_2$AgBiBr$_6$ which has a formula form of A$_2$BIB$_0$IIIX$_6$, can be considered as another type of 3D perovskite ABX$_3$.

However, it is worth noting that the 2D double perovskite structure, such as (BA)$_4$(AgBi)Br$_8$ ((100)—orientation), the octahedron formed by two metal cations is alternately arranged to form an inorganic layer, and then form 2D structure with large organic cation layer.

In recent years, great progress has been made in the preparation and application of 2D perovskite materials, such as the simple spin-coating method to prepare various perovskite films for photovoltaics, photodetectors, and other applications. However, the resulting polycrystalline film has a stability problem and is easily eroded by oxygen and humidity (Figure 1B). Therefore, it is very important to find an efficient method to prepare 2D single crystals with good air and humidity stability. Poglitsch and Weber first reported that 3D single-crystalline perovskites can be produced by cooling an HX-based solution containing perovskites in 1987. The preparation method of 3D perovskite single crystals has gradually matured: Huang's group applied a top-seeded solution growth (TSSG) method; Cheng's and Soek's groups used antisolvent-assisted crystalline methods; Bakr's group developed the antisolvent vapor-assisted crystallization (AVC) method; Liu's group discovered the inverse temperature crystallization (ITC) method; and so forth. For 2D perovskite, the growth of microcrystalline thin films (MCTFs) and nanocrystalline materials has been reported. However, although researchers put forth considerable effort, they failed to prepare large-area 2D single crystals.

In this review, the methods for preparing 2D perovskite single crystals have been summarized. Moreover, the device applications of 2D perovskite single crystals are discussed, and future research directions and developments are proposed.

2 | METHODS OF 2D PEROVSKITE CRYSTALLIZATION

The strategies and basic principles of 2D perovskite single-crystal growth are introduced. Some crystal formation mechanisms (steady nucleation rate and crystal growth rate) are given. In this review, the 2D perovskite refers to organic and inorganic lead halide 2D perovskite unless stated otherwise.

2.1 | Methods of preparation of 2D perovskite single crystals

The most widely used method to prepare organic-inorganic lead halide 2D perovskite single crystals is the solution process. Compared with the perovskite polycrystalline films, the growth of single crystal is more difficult and takes longer. The growth of single crystals is based on the solubility variation vs temperature or solvent content, but the conditions need to be well controlled. Several methods are introduced for the growth of 2D perovskite single crystals.

2.1.1 | Cooling HX-based precursor solutions/acid precipitation method

This method requires that the solubility of the perovskite in HX-based (X = Cl, Br, I) solutions is positively correlated with temperature. Poglitsch and Weber used this cooling method to grow 3D perovskite single crystals in 1987. They gradually decreased the temperature of an HX-based perovskite precursor solution from a high temperature (>90°C) to room temperature to obtain single crystals of 2D or 3D perovskite. The cooling rate affects the growth of single crystals greatly. By cooling the boiling HX-based precursor to room temperature, a series of homologous 2D perovskite crystals, such as...
(CH3(CH2)3NH3)2(CH3NH3)n−1PbnI3n + 1 ((BA)2(MA)n−1PbnI3n + 1) (n = 1, 2, 3, 4, ∞), were prepared by the Kanatzidis group. Rapid cooling leads to multiple nucleation sites with the formation of a large number of small crystals. Therefore, strict control of the cooling rate is important for obtaining high-quality, large, single crystals. Bakr’s group prepared (PEA)2PbI4·(MAPbI3)n–1 (n = 1, 2, 3) single crystals by cooling 90 °C precursor solutions to room temperature at a rate of 1 °C/h. The size of the single crystals reached the millimeter level (Figure 2A). However, when n is greater than 3, the 2D perovskite longer forms a single crystal, but grows in the form of a mixture, due to the large solubility difference between PEA and MA in the same solvent. Kanatzidis et al prepared millimeter-sized plate-like crystals of (3AMP) (MA)n−1PbnI3n + 1 and (4AMP)(MA)n−1PbnI3n + 1 by this cooling method (Figure 2B). By adding doped elements, doped 2D perovskite single crystals can be prepared by the cooling method. Han’s group obtained yellow flake-like crystals of (PEA)2PbBr4 and black flake-like crystals of Bi-doped (PEA)2PbBr4. Huang’s group synthesized large-area quasi-2D perovskite thin single crystals BA2MA2Pb3I10 by the space-confinned method. In perovskite precursor, perovskite ions form complexes with solvents. Nonwetting substrates differ from wetting substrates in that they are less attractive to the perovskite ions in the attraction complex, and thus the horizontal transport of ions along the confined space can be improved, which is beneficial for the large-scale growth of 2D perovskite in the horizontal direction (Figure 3H-K). Fu’s group prepared (BA)2(MA)n−1PbnX3n + 1 (n = 1, 2, 3) single-crystal films with millimeter lateral size and nanometer thickness by modifying the growth method of the space-constrained aqueous solution. The precursor is an HI-based solution. When the H2O and HI in the precursor on two substrates are completely evaporated at 80 °C, 2D perovskite single crystal membranes can be obtained.

2.1.2 Induced peripheral crystallization method/space-confined method

The induced peripheral crystallization (IPC) method proposed by Liu’s group utilizes prior edge evaporation to create seed crystals. The solubility of perovskite in γ-butyrolactone (GBL) solvent increases with temperature (Figure 3A,B). Perovskite single crystals prepared by conventional methods are usually in bulk form, but IPC method provides a good way to prepare single crystal membranes with controllable thicknesses and growth in the parallel orientation (Figure 3E). The apparatus for IPC is simple: a uniform substrate, a top glass, and a thermostat. The prepared saturated solution is dropped onto the preheated substrate, covered with the top glass, and placed at a constant temperature. When GBL volatilizes at the edge of the two glass plates, the inner solution is sealed by the edge crystals. At this time, when the temperature decreases, the solubility of perovskite decreases and crystal growth begins at the edge (the specific steps are shown in Figure 3D). Using this method, Liu’s group grew (PEA)2PbI4 single-crystal membranes (SCMs) on glass and polyethylene terephthalate (PET) substrates, and the size of the single crystals reached centimeters (>75 × 35 mm²) (Figure 3C). This IPC method limits the growth height of the single crystal in a confined space to obtain 2D perovskite single crystals on the flexible substrate (PET) (Figure 3F,G). Therefore, it is feasible to apply it to flexible devices. As the temperature decreases, the solubility of perovskite decreases to supply the growth of precipitated crystals. However, cooling too quickly will lead to multiple crystal nucleation sites, so large perovskite single crystals cannot be obtained.

Huang’s group synthesized large-area quasi-2D perovskite thin single crystals BA2MA2Pb3I10 by the space-confinned method. In perovskite precursor, perovskite ions form complexes with solvents. Nonwetting substrates differ from wetting substrates in that they are less attractive to the perovskite ions in the attraction complex, and thus the horizontal transport of ions along the confined space can be improved, which is beneficial for the large-scale growth of 2D perovskite in the horizontal direction (Figure 3H-K). Fu’s group prepared (BA)2(MA)n−1PbnX3n + 1 (n = 1, 2, 3) single-crystal films with millimeter lateral size and nanometer thickness by modifying the growth method of the space-constrained aqueous solution. The precursor is an HI-based solution. When the H2O and HI in the precursor on two substrates are completely evaporated at 80 °C, 2D perovskite single crystal membranes can be obtained.

Song’s group adopted an inkjet printing method in which they formed perovskite seeds on the substrate, put the seed stamp on the solution added to the substrate,
FIGURE 3  Legend on next page.
and grew perovskite single crystal films at a fixed site (Figure 3L). This method is applicable to the growth of various perovskite monocrystalline films and can change the distribution of perovskite precursor ions by affecting mass transport, thus effectively inhibiting random nucleation. The growth location of the single crystal film is related to the seed, and random single-crystal growth is inhibited.

2.1.3 | AVC method

The AVC method proposed by Cheng’s and Soek’s groups, also known as the solvent engineering approach and fast crystallization deposition, is used to prepare perovskite films. By taking advantage of the solubility difference of perovskite in different solvents, the perovskite was dissolved in solvents with high solubility (such as N,N-dimethylformamide [DMF], DMSO, GBL), and the antisolvent with low solubility (such as chlorobenzene, benzene, diethylether) was transported to the solution to promote crystallization (Figure 4A). Ren’s group reported the preparation of (PEA)$_2$PbBr$_4$ perovskite single crystals by the AVC method. DMF was used as the solvent of (PEA)$_2$PbBr$_4$ precursor solution which was stored in an atmosphere of chlorobenzene vapor. After several days, millimeter-sized (PEA)$_2$PbBr$_4$ 2D perovskite single crystals could be synthesized by controlling the rate of the antisolvent vaporization (Figure 4B-E). The key point of this approach is to find the optimal rate of the antisolvent vaporization. Evaporation that is too fast will cause multiple crystal nucleation sites and even affect the crystal quality, while evaporation that is too slow will prolong the growth cycle. In Deleporte’s group, (PEA)$_2$PbI$_4$ single crystal was prepared by combining the AVC method with a “space-confined” method as the “Antisolvent Vapor-assisted Capping Crystallization” (AVCC) method (Figure 4F,H). The crystallization of (PEA)$_2$PbI$_4$ perovskite with GBL as the solvent and dichloromethane (DCM) as the antisolvent is better than that with DMF as the solvent (Figure 4G,I).

2.1.4 | Slowly evaporating at constant temperature/controlled-evaporation method

With the solvent evaporating, the concentration of the solute increases gradually. When the concentration reaches the critical saturation concentration, the solute begins to precipitate, which is the principle used in the controlled-evaporation method. As the solute continues to evaporate, the solute continues to crystallize. The solute concentration remains at the saturated state for subsequent continuous crystallization.

Based on this simple physics principle, Raghavan et al grew RP phase (BA)$_2$(MA)$_{n-1}$Pb$_n$I$_{3n+1}$ ($n=1, 2, 3$) by solution-growth technique of slowly evaporating at constant temperature (SECT). The scale of single crystal is up to millimeter and has good crystallinity and spectral uniformity. Liu’s group utilized the controlled this evaporation method to fabricate (PEA)$_2$PbBr$_4$ 2D perovskite single crystals at room temperature. By controlling the rate of solvent evaporation at a fixed temperature, a nucleation seed forms in a gradually oversaturated solution. The next step is to control the growth conditions to prevent the formation of other nucleation seeds and ensure a large crystal is growing from the existing nucleation seed. With the temperature fixed at 23 ± 0.5°C, centimeter-sized ($≈27 \times 11$ mm$^2$) (PEA)$_2$PbBr$_4$ 2D perovskite single crystals (Figure 4J-M) can be obtained in the DMF-based precursor after 20 days. By studying the growth process of single crystals, they found the process is divided into two stages: there is no crystal formation in the first stage, where only the solvent evaporates; in the second stage, the solution becomes oversaturated and crystallization is observed, with the rate of the solvent (DMF) vaporization lower than its counterpart was in the first stage. At the same time, the fixed growth temperature of the single crystals needs to be optimized. If the
temperature is raised to 30°C, a large number of stacked crystallites will be produced.

### 2.1.5 Surface-tension-controlled crystallization

Via the difference between the growth rate on the surface of the solution and the growth rate in the solution, Liu’s group obtained some inch-sized single-crystal blocks (Figure 5F). By using the same solute and solvent as those in the IPC method and using different methods to control the surface tension and a hot stage, (PEA)$_2$PbI$_4$ block crystal with a regular shape was grown (Figure 5A-C). The solubility of (PEA)$_2$PbI$_4$ materials in γ-butyrolactone (GBL) solvent increases with increasing temperature. With decreasing temperature (cooling rate of 0.5°C/h from 95°C), the solubility of (PEA)$_2$PbI$_4$ in the prepared solution...
decreases, and the crystal grows on the surface of the solution due to the fast transfer at the surface (Figure 5D). The growth rate on the solution surface is higher than that in the solution. As the temperature drops further, the crystals grow so that the weight of the crystals exceeds the buoyancy, and the crystals sink completely into the solution, falling to the bottom of the bottle (Figure 5E). The cooling process continues down to \(30^\circ C\), and large crystal blocks of regular shape can be obtained.

Priya’s group prepared a series of perovskites \((\text{C}_4\text{H}_9\text{NH}_3)_n(\text{CH}_3\text{NH}_3)_1\text{PbnI}_{3n+1} (n = 1, 2, 3, 4, \infty)\) from 2D to quasi-2D and then 3D, and studied the nucleation mechanism at the air-water interface in 2016.\(^{82}\) The nucleation rate at the surface of the solution is greater than that in the solution. This conclusion is also confirmed in the 3D perovskite.\(^{83}\)

### 2.2 Models of the crystal growth

Crystal growth in supersaturated solution can be divided into two stages: (a) the formation of the crystal nucleus; and (b) the formation of a large single crystal by the continuous growth of the crystal nucleus. The nucleation stage in perovskite crystals is largely different from the classical nucleation in solidification. In solidification,
molecules come together to directly form a crystal nucleus, which can be totally reversed to molecules if the experimental condition reverses. However, molecules assemble to form irreversible micelles, and then the micelles join together to form a reversible crystal nucleus in perovskite crystallization. The second stage, which affects the quality of single crystals, is controlled by two aspects: (a) the solute diffuses to the crystal surface in the

**FIGURE 6** Legend on next page.
solution, and (b) the solute deposits on the crystal surface.

By using density functional theory (DFT) and classical nucleation theory, the crystallization phenomenon can be further understood. The crystallization process is divided into two stages, nucleation and crystal growth, corresponding to the model of single crystal suitable for solution growth described below.

2.2.1 | The steady-state nucleation rate

When the solution is oversaturated, the solute will precipitate out to form small micelles, and the micelles assemble to form a nucleus. Therefore, by vaporizing the solute or changing the temperature, we can control the solution to reach the oversaturated state and thus obtain the seed crystals and make the crystal grow. Equation (3) is used to describe the stable nucleation rate on the substrate.

\[ \nu = \omega \Gamma N_0 \exp \left( - \frac{\Delta G}{k_B T} \right) \]  (3)

where \( \nu \) is the steady nucleation rate, \( \omega \) is the frequency at which the solute molecules diffuse from the solution to the critical nucleus, \( \Gamma \) is the nonequilibrium Zeldovich factor, \( N_0 \) is the density of adsorption sites on the crystal surface, \( \Delta G \) is the Gibbs free energy change for the nucleus formation, also known as the nucleation barrier, \( k_B \) is the Boltzmann constant, and \( T \) is the solution temperature.

From Equation (2), the nucleation rate is affected by many factors and can be divided into two parts: the exponential part \( \exp \left( - \frac{\Delta G}{k_B T} \right) \) and the nonexponential part \( \omega \Gamma N_0 \). The value of \( \omega \Gamma N_0 \) depends on the supersaturation of the solution. When temperature is the main regulating factor of single crystal growth, the influence of the exponential part on the rate is dominant, and the influence of the nonexponential part can be ignored as a constant.

As the crystal grows, the exponential part changes with temperature.

The driving force in the crystallization process of a supersaturated solution is related not only to the thermodynamic temperature, but also to the natural logarithmic ratio of the concentration of the supersaturated solution. Regardless of the concentration of the solution, there are small grains precipitated and dissolved in the solution. When the solution is in the supersaturation region, the precipitation is larger than the dissolution, which will immediately cause the formation of small grains with more defects. As it enters the unsaturated zone, precipitation is less than dissolution, and the resulting crystal begins to slowly dissolve in solution. Therefore, it is crucial to control the proper solution concentration on the solubility curve: when the concentration is higher than saturation at a temperature, the nucleation rate increases sharply, and when the concentration is below saturation, the nucleation rate is zero (Figure 6A). When the supersaturation is higher, the nucleation rate is faster. The mass change of the precursors with evaporation time is recorded while forming single crystal (PEA)\(_2\)PbBr\(_4\) with the controllable evaporation method. The mass loss curve is clearly divided into two segments, and no crystallization is found in the first part (Figure 6B,C). In the second part, the solution is supersaturated and crystallization is observed. The intersection of these two lines is the critical concentration of nucleation. By controlling the temperature to a certain fixed value, the crystal growth rate remains stable, thus obtaining high-quality single crystals.

In the surface-tension-controlled crystallization method, an interesting phenomenon has been observed experimentally-the formation of a single crystal film on the surface of the solution in the initial state. This is easily explained by a simplified model of a single solute A and a single solvent S. A nanocrystallite contains many solute S molecules, which are the essence of the forming nucleus. It is assumed that a molecule A and j molecules...
S can form an A-Sj complex in the solution through the complex binding energy \( (E_c) \). The concentration of A-Sj complex is relative to the energies of A \( (\varepsilon_A) \), S \( (\varepsilon_S) \), and the cohesive energy \( (\varepsilon) \), which is determined by the surface energy \( (\gamma) \). The molecules are subjected to surface tension on the surface of the solution, and \( E_A + \varepsilon_A < 0 \) and \( \varepsilon_S > 0 \) respectively. The nucleation barrier in solution can be expressed as \( \Delta G_{\text{Solution}} \):

\[
\Delta G_{\text{Solution}} = \frac{16\pi}{3}\left(\frac{\gamma^3}{(e-e_A + k_BT\ln N_A)^2}\right)
\]

where \( \gamma \) is the surface energy of crystallite, \( e \) is the cohesive energy, \( e_A \) is the energy of the A-molecule, \( N_A \) is the mole fraction of isolated A, and \( e_\text{surf} \) is the surface tension-related elastic energy per A-molecule in the surface layer. On the surface of the solution, the decrease of the A-molecules is due to the surface tension, making \( e_\text{AS} = e_A - e_\text{surf} \), and \( e_\text{surf} > 0 \). Equations (4) and (5) show that the nucleation barrier in solution, \( \Delta G_{\text{Solution}} \), is larger than that at the surface \( \Delta G_{\text{Surface}} \) (Figure 5A, Figure 6H-J). By combining Equations (4) and (5) with Equation (3), the nucleation rate on the surface of the solution, \( k_\text{surf} \), is higher than that in the solution, \( k_\text{Solution} \), so the solvent molecules will form the film on the solution surface first. The existence of surface tension leads to the reduction of surface molecules, which reduces the nucleation barrier and molecular binding energy of the crystal, and the nucleus is formed on the solution-air surface and can serve as a template to guide subsequent crystal growth.

### 2.2.2 The crystal growth rate

The steady-state nucleation rate is used to predict the deposition of micelles on the crystal surface on the microscopic scale, and the crystal growth rate is used to control the crystal growth from the macroscopic change of crystal quality. The growth rate of the crystal determines the quality of the crystal. There is a general understanding that the lower the growth rate, the better the quality of the crystal. That is why perovskite films fabricated by spin coating are polycrystalline—the solution in spin coating has a high nucleation rate (multipoint nucleation) and high crystal growth rate (limited grain size).

The continuous growth of crystal includes two processes: solute diffusion from the solution to the crystal surface and solute deposition on the crystal surface. The diffusion rate in the former is an important factor (the diffusion rate varies exponentially with the temperature). For a solution system, control of the diffusion rate can be achieved by controlling the temperature. The solute deposition process is more difficult to control than the diffusion rate. Crystalization kinetics shows that when solute concentration is controlled above the solubility curve (when slightly oversaturated), high-quality crystals can be grown on already-formed crystals or seeds without excess nucleation (nucleation point). According to the oversaturation model in Equation (6), the growth rate of the crystal mass is directly proportional to the first-order derivative of solubility and the temperature ramp rate.\(^1\):

\[
\frac{dm}{dt} = \frac{1}{2}V\frac{dC(T)}{dT}\frac{dT}{dt}
\]

where \( m \) is the mass of the crystal, \( C \) is the solution concentration, and \( V \) is the volume of the solution, which changes very little throughout the crystallization process, so it can be regarded as a constant.

Take the example of (PEA)\(_2\)PbI\(_4\) single crystals growing by the induced-peripheral-crystallization (IPC) method of cooling GBL-based precursor solution. The solubility of (PEA)\(_2\)PbI\(_4\) in GBL is positively proportional to temperature (Figure 6K),\(^73\) and its first derivative with respect to temperature is fitted and shown in Figure 6L. Figure 6L shows that the second derivative of solubility changes greatly from \( 3.45 \times 10^{-4} \) to \( 8.47 \times 10^{-4} \) with respect to temperature near 75°C. By choosing 25°C to 80°C as the temperature range, the first derivative of solubility with temperature can be expressed as \( \frac{dC(T)}{dT} = kT + b \)\(^73\):

\[
\frac{dC(T)}{dT} = kT + b
\]

where \( k \) is approximately a fixed value of \( 3.45 \times 10^{-4} \), and \( b \) is the intercept of the fitting line with a fixed value.

| Materials | Excitation wavelength \( \lambda \) (nm) | Emission peak (nm) |
|-----------|----------------------------------------|--------------------|
| (PEA)\(_2\)PbBr\(_4\)\(^3\) | \( \lambda < 350 \) | 407 |
| | \( 350 < \lambda < 375 \) | 407-412 |
| | \( \lambda > 37 \) | 412-407 |
| (PEA)\(_2\)PbI\(_4\)\(^73\) | \( \lambda < 400 \) | 525 |
| | \( 400 < \lambda < 800 \) | 525-530 |
| | \( \lambda > 800 \) | 530-520 |
The temperature drop rate is fixed at a constant value of $1^\circ C\, h^{-1}$. Since the volume, $V$, and the rate of temperature change with time, $dT/dt$, during crystal growth can be regarded as constants, the change of crystal mass with time depends on the value of the first derivative of solubility with respect to temperature in solution. Therefore, the crystal growth rate can be simplified as $73$:

$$\frac{dm}{dt} = AkT + b$$

where $A$ is a simplified constant.

As the temperature drops from $80^\circ C$ to $25^\circ C$ at a rate of $1^\circ C\, h^{-1}$, the rate of crystal growth is slowing. The decreasing growth rate can not only produce high-quality single crystal, but also restrict the growth of single crystal thickness, control the growth rate in different directions, and make the single crystal grow along the side selectively.$77$ High-quality single crystals can be obtained by choosing the proper temperature ramp rate. Because the temperature of the solution can be well controlled, the growth of high-quality single crystals can be obtained.$73$

Most of the preparation of single crystal is by the solution method. By adjusting the temperature, the solution concentration can be maintained at a slightly supersaturated condition, so as to obtain high-quality single crystal. However, the controlled-evaporation method keeps the solution concentration in the supersaturated zone while the crystal grows (the solvent decreases) and the solvent evaporates continuously (at a certain temperature). At the beginning, the solution concentration is lower than the solubility and in the unsaturated zone. From Figure 6B, it can be seen that at $23^\circ C$, the solvent evaporation rate changes from $3.77$ to $2.78$ mg/h, and the solution concentration changes from $0.873$ to $1.073$ g/mL.$29$ The intersection of the two lines in Figure 6B is the critical saturation of the solution at $23^\circ C$, which indicates that the solution is in the slightly supersaturated region when the crystal is growing.

Regardless of the growth method, a stable growth rate is important for obtaining high-quality single crystals. Whether through temperature regulation or solvent evaporation, it is based on the regulation of the solubility curve region corresponding to the solution concentration. Maintaining a slightly supersaturated solution concentration inhibits excessive nucleation while preventing the dissolution of the already-grown nuclei and achieves a slower growth rate.

### 2.3 Applications of 2D perovskite single crystals

2D perovskite single-crystal not only has the excellent photoelectric properties of three-dimensional perovskite, but also has better moisture resistance because of its...
larger hydrophobic organic cation group, making it a better choice for various devices, such as memory and photodetectors. Several applications of 2D perovskite single-crystals are summarized in the following section.

2.3.1 Optoelectronic properties

In this section, we introduce some fundamental optoelectric properties of semiconductor materials that are of great benefit to the rational application of 2D perovskite single crystal materials. Because they have fewer grain boundaries and defects, single crystals have better optoelectric properties than MCTFs, such as lower trap density, longer carrier lifetime, and so forth.

Electrical properties

The trap-state density \( n_{\text{trap}} \) is the key parameter of semiconductor material quality. The lower the value, the better quality of the perovskite single crystal. To evaluate the quality and electrical properties of perovskite single crystals, the space charge limited current (SCLC) method is used by measuring the current-voltage \( (I-V) \) characteristics in the dark. This curve is divided into three regions: (a) The electrode is in ohmic contact with the perovskite, and the current changes linearly with the voltage; (b) the current increases nonlinearly with the change of voltage. At this stage, the trap states inside the perovskite are filled with injected carriers; and (c) the current is proportional to the square of the voltage, when the carrier drift velocity is saturated. There is a kink point at the intersection of the ohmic region and the trap-filled limit area. At this time, the trap states inside the material are just filled by the injected carriers, and there are no excess injected carriers. Therefore, \( n_{\text{trap}} \) can be calculated from the trap-filled limit voltage \( (V_{\text{TFL}})^{92.93} \):

\[
V_{\text{TFL}} = \frac{en_{\text{trap}}L^2}{2\varepsilon_0\varepsilon}
\]

where \( e \) is the electron charge, \( L \) is the device thickness, \( \varepsilon \) is the relative dielectric constant of the perovskite, \( \varepsilon_0 \) is the vacuum permittivity, and \( n_{\text{trap}} \) is the electron-trap density or hole-trap density, depending on whether it is an electron-only device or a hole-only device.

The carrier lifetime \( (\tau) \) is the lifetime of the nonequilibrium carriers produced by photoinjection and electroinjection, reflecting the crystal defects, and is defined as the average time of carrier existence. The equation is\(^{88}\):

\[
\frac{1}{\tau} = \frac{1}{\tau_r} + \frac{1}{\tau_{\text{nr}}}
\]

where \( \tau_r \) is the radiative lifetime, and \( \tau_{\text{nr}} \) is the non-radiative lifetime. The main factors affecting the lifetime of nonequilibrium carriers are the recombination mechanisms of carriers (direct recombination, indirect recombination, surface recombination, Auger recombination, and so forth). The recombination centers caused by harmful impurities and defects in materials greatly influence the nonequilibrium carrier lifetime. In order to increase the nonequilibrium carrier lifetime, harmful impurities and defects should be removed. Single-crystalline materials have fewer defects and thus have longer lifetimes than MCTFs.\(^{73}\)

Transient absorption spectra and time-resolved fluorescence spectra are applied to measure the fluorescence lifetime. The longer the fluorescence lifetime, the fewer defects and the better crystallinity of the material.

Carrier mobility, \( \mu \), is an important parameter of semiconductors, and it describes the motion of carriers in an electric field. Two pathways can take to measure \( \mu \): one utilizes the \( I-V \) curve of the SCLC, from which it can be calculated according to Mott’s SCLC theory in the third stage\(^3,94\); the second is to determine the type of semiconductor conduction, as well as the concentration and mobility of the majority carriers by the Hall effect.

Optical properties

By analyzing the absorption spectrum, we can determine the absorption onset and bandgap of the \((\text{PEA})_2\text{PbX}_4\) single crystals. For example, when \( X \) changes from Br to I, the absorption onset of the absorption spectrum redshifts from 428 nm to 550 nm, which means that \((\text{PEA})_2\text{PbI}_4\) has a wider range of visible light absorption than \((\text{PEA})_2\text{PbBr}_4\).\(^{33}\) The position of the valence band edge relative to the vacuum energy level can be estimated by using the results of ultraviolet photoelectron spectroscopy (UPS) measurements. Combining this with the bandgap, the value of the conduction band edge can be further obtained.

The photoluminescence (PL) quantum yield is defined as the ratio of the number of photons emitted by a luminous substance after absorption to the number of photons absorbed from the excitation source. The smaller the full width at half maximum (FWHM) of the PL spectra, the better consistency of the substance and the higher color purity and narrower emission bandwidth of the sample. Dou et al showed that the stable PL peak of 2D perovskite single crystal varies with the thickness of the single crystal.\(^{95}\) When the thickness of the single crystal increases, the blue shift trend appears in PL peak.

It is worth noting that the emission peaks of both \((\text{PEA})_2\text{PbBr}_4\) and \((\text{PEA})_2\text{PbI}_4\) shift with the change of the excitation wavelength. This characteristic feature can also
be observed in MCTFs (Table 2).33, 73 (Table 3) summarizes basic optoelectronic properties of single crystal (SC), microcrystalline thin film (MCTF), and nanoplates of (PEA)2PbI4 and (PEA)2PbBr4. Raghavan et al explored homologous (BA)2(MA)n−1PbnI3n+1 (n = 1, 2, and 3) materials, and they believed that the low-threshold lasing behaviors with different emission wavelengths at room temperature might be the cause of this phenomenon.80

2.3.2 Solar cells

At present, 3D perovskite polycrystalline or nanocrystalline thin films are mostly used as the light absorption layers in PSCs, and the device power conversion efficiency (PCE) has already exceeded 25%.1 However, a number of key problems, such as the lack of resistance to water, light and heat, and many grain boundaries and defects of polycrystalline and nanocrystalline thin films, have hindered large-scale industrial production of PSCs. PSCs with single-crystal thin film as the light absorption layer have mainly been constructed with MAPbI3, 96 and MAPbBr3.6, 97, 98 Although the PCE of 3D single-crystal PSCs has increased rapidly to 21.09% in the past 23 years, it is still far lower than that of polycrystalline silicon cells.99–101 For pure 2D perovskite single-crystals, however, the wide band gap (>2.3 eV) makes them less suitable for photovoltaic applications.102 Karunadasa’s group first proposed the method of mixing 2D perovskite with conventional 3D perovskite in a single absorption layer to overcome the high bandgap value, reduce the exciton binding energy, and improve the efficiency of charge collection.61 They applied (PEA)2PbI4·(MAPbI3)2 as the light absorption layer. And the PCE was 4.73% (AM1.5G) with \(V_{oc} \) of 1.18 V. Meanwhile, the device exhibited good stability for over 46 days in air at a relative humidity level (RH) of 52%. In the study of homologous \((\text{CH}_3\text{NH}_3)_2\text{Pb}_5\text{I}_{16} (n = 5)\) family, Stoumpos et al showed that when \(n < 5\), the crystal is more likely to grow freely along the plane of the inorganic layer and grows slowly in the direction of vertical accumulation; when \(n = 5\), the crystals appear to accumulate vertically (Figure 7C).103 The DFT calculation of the noncentrosymmetric crystal showed that BA2MA4Pb3I16 is a direct band gap with or without spin-orbit coupling (SOC) (Figure 7A,B). By using the hot-casting device fabrication process, the prefabricated BA2MA4Pb3I16 crystals were redissolved in DMF to achieve a planar photovoltaic device, and the PCE reached 8.71% (Figure 7D-F). Overall, the quasi-2D perovskites are used to improve the charge collection efficiency of PSCs, and enhance the device stability under environmental conditions.37, 53, 104, 105

| Materials              | Bandgap or absorption on set | Valence band edge (eV) | PL peak FWHM (nm) | PL quantum yield (cm^−3) | PL quantum yield (%) |
|------------------------|-----------------------------|-----------------------|-------------------|--------------------------|----------------------|
| (PEA)2PbI4            | SC-membrane                 | 550 nm                | 2.28 eV           | 525 nm FWHM = 15.1 nm    | 34.5%                |
|                        | single crystal              | 550 nm                | 2.35 eV           | 526 nm FWHM = 21.9 nm    | 22%                  |
|                        | MCTF                       | 550 nm                | 2.34 eV           | 520.5 nm FWHM = 21.9 nm  | 10%                  |
|                        | Nanoplates (0.38 μm)        | 550 nm                | 2.35 eV           | 525 nm FWHM = 21.9 nm    | 26%                  |
| (PEA)2PbBr4           | SC-membrane                 | 428 nm                | 2.91 eV           | 410 nm FWHM = 14 nm      | 26%                  |
|                        | single crystal              | 428 nm                | 2.91 eV           | 410 nm FWHM = 14 nm      | 26%                  |
|                        | MCTF                       | 428 nm                | 2.91 eV           | 410 nm FWHM = 14 nm      | 26%                  |
|                        | Nanoplates (0.38 μm)        | 428 nm                | 2.91 eV           | 410 nm FWHM = 14 nm      | 26%                  |
In addition, since the orientation of spin-coated polycrystalline films is random, many efforts have been made to optimize the crystal orientation and increase the grain size to reduce the effect of defects on solar cell performance. For 2D perovskite crystal growth, it is better to make the grain orientation more favorable for carrier transport. However, the growth direction of 2D RP phase perovskite single crystal (n < 5) tends to grow along (00 hour) plane preferentially. Therefore, it is worth exploring the method of directly growing quasi-2D single crystal with favorable electron and hole transport direction to reduce defects and improve device performance. Moreover, the synthesis of n > 5 (the growth direction of the trend in the horizontal and vertical

![Figure 8](image-url)
direction is not large) quasi-2D perovskite single crystal should also be tried.

2.3.3 Memories

Ren’s group used 2D Ruddlesden Popper phase hybrid lead bromide perovskite single crystals [(PEA)$_2$PbBr$_4$ with bandgap of $\sim$2.9 eV) as materials for low-working-current nanodevice applications. The 2D perovskite single crystal is fabricated by the AVC method, stripped into thin layers and combined into a graphene/2D crystal/Au vertical structure to study the electrical properties in resistance memory elements (Figure 8A). Monte Carlo simulations based on Br$^-$ ions and vacancy movement to form filaments supported the TEM observations (Figure 8B-D). The resistive memory has the lowest operation current (10 pA, Figure 8E), which can overcome the disadvantage of the large dark current of the current resistive memory materials, such as HfO$_x$, AlO$_x$, TaO$_x$, TiO$_x$, MoS$_2$, and so forth (Figure 8F). In addition, the memory also demonstrated 400 fJ/spike synaptic operation, very close to the

**FIGURE 9** A and B, Schematic illustrations of the photoelectric process and photoconductivity gain in the Au/(PEA)$_2$PbI$_4$ SCM/Au device under light illumination; C, The current-voltage (I-V) curves of the device measured in the dark and under 460-nm wavelength illumination with various light intensities; D, EQE and $D^*$ for the photosensor with the incident light power density ranging from $8 \times 10^{-5}$ to 310 mW cm$^{-2}$ at a wavelength of 460 nm under a fixed 4 V bias; E, Absorbance spectrum of the (PEA)$_2$PbI$_4$ SCM and photoresponse spectrum of the photosensor illuminated using monochromatic light with wavelength ranging from 350 to 650 nm at 4 V bias; F, Temporal photocurrent response of the (PEA)$_2$PbI$_4$ SCM photosensor; G, Schematic diagram of the photodetector made using a (PEA)$_2$PbBr$_4$ single crystal; H, Voltage-current curves of the (PEA)$_2$PbBr$_4$ device illuminated using a 365-nm LED at different light intensities; I, Transient photocurrent of the photodetector at a bias of 10 V

Source: A-F, Reproduced with permission: Copyright 2018, Springer Nature Publishing AG. G-I, Reproduced with permission: Copyright 2019, The Royal Society of Chemistry
energy consumption of biological synapses. Therefore, the 2D perovskite single crystal can be used to realize very low energy consumption in neuromorphic computation for massively parallel information processing similar to that of the human brain. In the future, the back-propagation neural network based on a 2D perovskite resistance memory array will have extremely high energy efficiency, which is the basis of high-performance and low energy applications.

### 2.3.4 Photodetectors

Due to the excellent optical properties, including fluorescence and exciton effects, of 2D perovskite single crystals, they are more widely used to make high-performance photodetectors with high responsivity and low dark current.

Peng’s group reported the first photodetector based on 2D (C4H9NH3)2PbBr4 perovskite crystals.109 The perovskite crystals with the domain size of several to tens of micrometers and the thickness of tens of nanometers (Figure 8I) were synthesized using a solution-processed method and grown on arbitrary flat substrates. Then, the photodetectors were formed with single-crystalline graphene films as the source-drain top electrodes (Figure 8G—8 hours). When the incident wavelength is below 510 nm (photon energy 2.43 eV), the photocurrent of the device was very large and generated obvious response. At the same time, the optical response of the device depended on the variation of incident optical power and bias voltage. The devices possessed extremely low dark current (≈10⁻¹⁰ A), a high ON/OFF current ratio (up to 10³), and high responsivity (≈2100 A/W) (Figure 8J-L).

Liu’s group reported an “induced peripheral crystallization” (IPC) method to fabricate a large-area (73 × 35 mm², exceeding 2500 mm², 0.6 μm thickness) 2D (PEA)2PbI4 perovskite single-crystalline flexible membrane for photosensors in 2018.73 According to the oversaturation model and the plot of the first-order derivative with respect to temperature of (PEA)2PbI4, the temperature ramp rate is regulated to 1°C h⁻¹ for growing single crystals along lateral dimensions and limiting the growth thickness. The structure of the flexible photosensors is Au/crystal/Au, and they exhibited very high external quantum efficiency (EQE) of 26 530%, responsivity (R) of 98.17 A W⁻¹ and detectivity (D*) as high as 1.62 × 10¹⁵ cm·Hz¹/₂ W⁻¹ (Jones) (Figure 9A-F).

In the same year, Liu’s group reported another method called the “controlled-evaporation method” utilizing a controlled-evaporation process to grow well-defined large-size (exceeding 200 mm²) 2D (PEA)₂PbBr₄ single crystals.33 According to the model of the steady-state nucleation rate, the optimized single-crystal growth
temperature is 23 ± 0.5°C. Planar-type UV photodetectors based on (PEA)$_2$PbBr$_4$ single crystals with Au interdigitated electrodes showed excellent detection performance, such as extremely low dark current, high ON/OFF ratio and detectivity, and fast response rate (shown in Table 4) (Figure 9G-I). Additionally, the environmental and irradiation stability are excellent as shown through humidity testing and UV-source switch testing. The performance of this UV detector is the best among the detectors using zinc oxide (ZnO), titanium dioxide (TiO$_2$), and other state-of-the-art materials, which paves the way for ultrafast optical computing and optical communications using the large-size, high-quality single-crystal materials.

### 2.3.5 Field-effect transistors

The layered structure of 2D and quasi-2D perovskite results in carrier transport anisotropy. The mobility of carriers in the layered plane composed of inorganic octahedrons is much higher than that perpendicular to the plane (the tunneling probability of carriers through interlaminar organic macromolecules is lower). By taking advantage of this material property, field-effect transistors (FETs) can be made with a surface channel as the transport path. The majority of FETs using perovskite single crystals are 2D FETs due to restriction of the 3D material thickness. Chen’s group fabricated a series of 2D FETs using (BA)$_2$ (MA)$_{n-1}$Pb$_n$I$_{3n+1}$ ($n = 1, 2, 3$) in

**Figure 10**

A. Optical image of the exfoliated (BA)$_2$(MA)$_{n-1}$Pb$_n$I$_{3n+1}$ with Ag contacts. B-D. Output characteristics of (BA)$_2$(MA)$_{n-1}$Pb$_n$I$_{3n+1}$ single-crystal FETs under various $V_{bg}$ values for B, $n = 1$, C, $n = 2$, and D, $n = 3$ at 77 K. E. Schematic illustration of the transport behavior of the (BA)$_2$(MA)$_{n-1}$Pb$_n$I$_{3n+1}$ perovskite crystal for $n = 1$ to $n = 3$. Red arrows and their corresponding shading indicate the direction of current flow and intensity in the conduction channel, respectively. Source: A-E, Reproduced with permission: Copyright 1999-2019, John Wiley & Sons, Inc. F. Optical images of graphene-protected (C$_6$H$_{14}$NH$_3$)$_2$PbBr$_4$ before cutting out a channel and after forming a device with graphene electrodes. Reproduced with permission: Copyright 2016, American Chemical Society. G. Optical image of an FET device based on (PEA)$_2$PbI$_4$. Reproduced with permission: Copyright 2018 Elsevier Inc. H. Optical image of an FET device based on (PEA)$_2$CsSn$_2$I$_7$. Reproduced with permission: Copyright 2018, American Chemical Society.
| Materials          | Preparation methods                                                                 | Device structure parameters | Transfer characteristics                                                                 | Mobilities (average) | On/off ratio | Subthreshold swing (SS) |
|--------------------|--------------------------------------------------------------------------------------|-----------------------------|------------------------------------------------------------------------------------------|----------------------|--------------|------------------------|
| MAPbI$_3$          | Two-step growth method, dry-transfer technique and thermal annealing (boron nitride [BN] layer) | Channel length 3 μm (no BN layer) Channel width 10 μm (no BN layer) | Unipolar n-type After thermal annealing, from unipolar n-type behavior to ambipolar behavior and finally to unipolar p-type behavior | 4 cm$^2$ V$^{-1}$ s$^{-1}$ (77 K) | n = 1, 10$^2$ | n = 3, 150 |
| (BA)$_2$(MA)$_n$Pb$_{3n+1}$I$_{3n+1}$ | Exfoliated from bulk crystals by a Scotch tape method and transferred to a silicon substrate | n = 3, 10 μm | Unipolar n-type | n = 1, 2, and 3 are 2 × 10$^{-3}$, 8.3 × 10$^{-2}$, and 1.25 cm$^2$ V$^{-1}$ s$^{-1}$ (77 K) | n = 1, 2, 10$^4$ | n = 3, 10$^6$ |
| (C$_6$H$_5$C$_2$H$_4$NH$_3$)$_2$Pb$_{3n+1}$I$_{3n+1}$ | Mechanical exfoliation (Scotch-tape micromechanical cleavage technique) | n = 3, 10 μm | Unipolar n-type | n = 1, 2, and 3 are 2 × 10$^{-3}$, 8.3 × 10$^{-2}$, and 1.25 cm$^2$ V$^{-1}$ s$^{-1}$ (77 K) | n = 1, 2, 10$^4$ | n = 3, 10$^6$ |
| (C$_6$H$_5$C$_2$H$_4$NH$_3$)$_2$SnI$_4$ | Spin-coated polycrystalline film | Channel length 95 μm Channel width 2 mm | n-type Near 1 cm$^2$ V$^{-1}$ s$^{-1}$ (related to electrodes) | 15 cm$^2$ V$^{-1}$ s$^{-1}$ (room temperature) | 2 × 10$^6$ | 1.1 ± 0.4 (Au electrodes) 1.1 ± 0.3 (Ag) 1.1 ± 0.2 (Al) |
| PEASnI$_4$ | Surface treatment with a self-assembled monolayer, top-contact/top-gate structure | Channel length 20 μm | n-type | Near 1 cm$^2$ V$^{-1}$ s$^{-1}$ (related to electrodes) | 15 cm$^2$ V$^{-1}$ s$^{-1}$ (room temperature) | 2 × 10$^6$ | 1.1 ± 0.4 (Au electrodes) 1.1 ± 0.3 (Ag) 1.1 ± 0.2 (Al) |
| (C$_6$H$_5$C$_2$H$_4$NH$_3$)$_2$CsSn$_2$I$_7$ | Bottom-gate, bottom-contact | Channel length 20 μm | n-type | Near 1 cm$^2$ V$^{-1}$ s$^{-1}$ (related to electrodes) | 15 cm$^2$ V$^{-1}$ s$^{-1}$ (room temperature) | 2 × 10$^6$ | 1.1 ± 0.4 (Au electrodes) 1.1 ± 0.3 (Ag) 1.1 ± 0.2 (Al) |
the RP phase (Figure 10A), and showed unipolar n-type carrier transport characteristics. As the material changes from 2D to quasi-2D (n value from 1 to 3), the carrier mobility increases (Figure 10E). This can also be seen in the output characteristic curves (Figure 10B-D). Li’s group also used the same material (BA)2(MA)n−1 Pb3I3n+1 (n = 3) to construct 2D FETs with controlled material phase purity through mechanical exfoliation.

Perovskite FETs are combined with the good light-absorbing properties of the material itself to produce photosensitive perovskite FETs. Peng’s group made the first 2D perovskite single crystal photodetector based on an FET structure (Figure 10F). Rand’s group used graphene to cover 2D I-containing perovskite single-crystal (PEA)2PbI4 to inhibit the spontaneous loss of iodine, reduce crystal degradation and improve the overall stability of the device (Figure 10G). In addition to I-based materials, there are also many Sn-based perovskite FETs, such as phenylethyl ammonium tin iodide (PEA)2SnI4 and alkyl ammonium tin iodide (CnH2n+1NH3)2SnI4 (n from 4 to 12). However, as Sn2+ is easily oxidized to Sn4+ in 2D perovskite, the environmental stability is worse than that of I-based perovskite, so the single-crystal devices are less reported. Li’s group prepared (C6H5C2H4NH3)2CsSn2I7 single-crystal FETs with millimeter size and high field-effect hole mobility and proved that the material lacked Sn4+ with high purity and high quality (Figure 10H).125 The introduction of large organic cations enhances the humidity resistance of perovskite and makes the device more stable. The structure of 2D materials is bound to be better than 3D counterparts in FET applications. Table 5 summarizes parameters of single-crystal perovskite-based FETs.

3 CONCLUSIONS AND OUTLOOK

2D perovskite single-crystal materials are receiving increasing attention because of their remarkable properties and superior potential in optoelectronic applications. Their most notable features are natural quantum wells and excellent moisture resistance compared with their 3D counterparts.

2D perovskite single-crystal materials have many excellent properties, including long fluorescence lifetime, fewer defects and high photoluminescence quantum yield. It is worth noting that 3D perovskite single-crystal offer the ability to change the elements at three sites (different organic groups, metals, halogens) and to adjust the components to obtain materials with different properties. On the contrary, 2D perovskite materials have two positions of organic molecules, which greatly increase the diversity of the materials. By changing the type of large organic cations, the band gap of 2D materials can be adjusted to obtain desired optoelectronic properties. Therefore, the diversity of 2D perovskite single-crystal elements can be used to obtain different material properties, which further extends the application range of 2D perovskite single-crystal materials.

For 2D perovskite single crystals, the future research directions can be considered from among the following:

1. For some 2D materials, existing fabrication methods require finding a specific solvent to dissolve perovskite. For example, in the IPC method, (PEA)2PbBr4 is dissolved in GBL, and the solubility increases with temperature. To use this method, one needs to find a solvent in which the solubility changes with temperature. Therefore, general solvents will be sought that can be used to make various perovskite single crystals.

2. The growth method needs to be further optimized to facilitate commercialization. Many growth methods of 2D perovskite single crystals have been discussed here, but all of them require a long time to grow large-area single crystals, so the growth time needs to be further optimize and shortened to facilitate future large-scale production.

3. The properties of 2D perovskite materials can be utilized to seek more device applications. The method of fabricating large-area flexible 2D perovskite single crystals paves the way for applications in high-performance, flexible, single-crystalline electronics and wearable devices including displays, touch sensing devices, transistors, and so forth. For 2D/3D mixed PSCs, it is worth exploring to find a method to directly grow quasi-2D perovskite single crystal to reduce defects and improve the power conversion efficiency. Regarding FETs, it has been reported that they are all made on 2D/quasi-2D perovskite single crystals below the millimeter level, so it is necessary to develop simple and large-area single-crystal membranes with controllable thickness for further FET applications.

ACKNOWLEDGMENT

This work was financially supported by National Natural Science Foundation of China (61604119, 61704131, and 61804111).

CONFLICT OF INTEREST

The authors declare no conflict of interest.

ORCID

Shengzhong (Frank) Liu https://orcid.org/0000-0002-6338-852X

REFERENCES

1. https://www.nrel.gov/pv/cell-efficiency.html. Accessed 20 May 2020.
2. Liu Z, Chang J, Lin Z, et al. High-performance planar perovskite solar cells using low temperature, solution-combustion-based nickel oxide hole transporting layer with efficiency exceeding 20%. Adv Energy Mater. 2018;8(19):1703432.
3. Zhang B, Su J, Guo X, et al. NiO/perovskite heterojunction contact engineering for highly efficient and stable perovskite solar cells. *Adv. Mater.* 2020;32(8):1903044.

4. Dong Q, Song J, Fang Y, Shao Y, Ducharme S, Huang J. Lateral-structure single-crystal hybrid perovskite solar cells via piezoelectric poling. *Adv. Mater.* 2016;28(14):2816-2821.

5. Ma J, Su J, Lin Z, et al. Improve the oxide/perovskite heterojunction contact for low temperature high efficiency and stable all-inorganic CsPbI2Br perovskite solar cells. *Nan Energy* 2020;67:104241.

6. Lee L, Baek J, Park KS, Lee Y, Shrestha NK, Sung MM. Wafer-scale single-crystal perovskite patterned thin films based on geometrically-confined lateral crystal growth. *Nat Commun.* 2017;8:15882.

7. Deschler F, Price M, Pathak S, et al. High photoluminescence efficiency and optically pumped lasing in solution-processed mixed halide perovskite semiconductors. *J Phys Chem Lett.* 2014;5(8):1421-1426.

8. Zhang Q, Ha ST, Liu X, Sum TC, Xiong Q. Room-temperature near-infrared high-Q perovskite whispering-gallery planar nanolasers. *Nano Lett.* 2014;14(10):5995-6001.

9. Liao Q, Hu K, Zhang H, Wang X, Yao J, Fu H. Perovskite microdisk microlasers self-assembled from solution. *Adv Mater.* 2015;27:3405-3410.

10. Wang K, Sun W, Li J, Gu Z, Xiao S, Song Q. Unidirectional lasing emissions from CH3NH3PbI3 perovskite microdisks. *ACS Photonics.* 2016;3(6):1125-1130.

11. Zhu H, Fu Y, Meng F, et al. Lead halide perovskite nanowires with low lasing thresholds and high quality factors. *Nat Mater.* 2015;14:636-642.

12. Nazarenko O, Yakunin S, Morad V, Cherniukh I, V Kovalenko M. Single crystals of caesium formamidinium lead halide perovskites: solution growth and gamma dosimetry. *NPJ Asia Mater.* 2017;9:e373.

13. Liu Y, Ren X, Zhang J, et al. 120 mm single-crystalline perovskite and wafers: towards viable applications. *Sci China: Chem.* 2017;60:1367-1376.

14. Liu Y, Sun J, Yang Z, et al. 20-mm-Large single-crystalline formamidinium-perovskite wafer for mass production of integrated Photodetectors. *Adv Opt Mater.* 2016;4:1829-1837.

15. Zhang Y, Liu Y, Li Y, Yang Z, Liu SF. Perovskite CH3NH3PbI3 (BrxI1-x) single crystals with controlled composition for fine-tuned bandgap towards optimized optoelectronic applications. *J Mater Chem C.* 2016;4:9172-9178.

16. Rose G. Ueber einige neue Mineralien des Urals. *J Prakt Chem.* 1840;19(1):459-468.

17. Kovalenko MV, Bodnarchuk MI. Lead halide perovskite nanocrystals: from discovery to self-assembly. *CHIMIA Int J Chem.* 2017;71(7-8):461-470.

18. Weber D, Naturforsch Z. CH3NH3PbX3 ein Pb (II)-system mit kubischer perowskitstruktur/CH3NH3PbX3 a Pb (II)-system with cubic perovskite structure. *B: J Chem Sci.* 1978;33:1443-1445.

19. Stoumpos CC, Kanatzidis MG. The renaissance of halide Perovskites and their evolution as emerging semiconductors. *Acc Chem Res.* 2015;48:2791-2802.

20. Zuo C, Bolink HJ, Han H, Huang J, Cahen D, Ding L. Advances in perovskite solar cells. *Adv Sci.* 2016;3(1):1500324.

21. Noriko OY, Takasuke M, Hiroshi S. Calorimetric and IR spectroscopic studies of phase transitions in methylammonium trihalogenoplumbates (II). *J Phys Chem Solid.* 1990;51:1383-1395.
44. Jacobson AJ, Johnson JW, Lewandowski JT. Interlayer chemistry between thick transition-metal oxide layers: synthesis and intercalation reactions of K[Ca2Nan-3NbnOn3n+1] (3 ≤ n ≤ 7). Inorg Chem. 1985;24:3727-3729.
45. Olga N, Robert KM, Michael W, Eduardo C-R, Sergii Y, Maksym VK. Luminescent and photoconductive layered halide perovskite compounds comprising mixtures of cesium and guanidinium cations. Inorg Chem. 2017;56:11552-11564.
46. Soe CMM, Stoumpos CC, Kepenekian M, et al. New type of 2D perovskites with alternating cations in the interlayer space, (C(NH3)2)3(CH3NH3)hPbI3n+1: structure, properties, and photovoltaic performance. J Am Chem Soc. 2017;139:16297-16309.
47. Cao D, Stoumpos CC, Farha O, Hupp J, Kanatzidis M. 2D homologous perovskites as light-absorbing materials for solar cell applications. J Am Chem Soc. 2015;137:7843-7850.
48. Su J, Zhang Z, Hou J, et al. Pressure-dependent mechanical and thermal properties of lead-free halide double perovskite Cs2AgBr6: A new direct band gap material. J Phys Chem Lett. 2019;10(5):1120-1125.
49. Slavney AH, Hu T, Lindenberg AM, Karunadasa HI. A bismuth-halide double perovskite with long carrier recombination lifetime for photovoltaic applications. J Am Chem Soc. 2016;138(7):2123-2141.
50. Snoeck G, Haghhighirad AA, Milot RL, et al. CsJInAgCl6: a new lead-free halide double perovskite with direct band gap. J Phys Chem Lett. 2017;8(4):772-778.
51. Lecardi F, Cirignano M, Baranov D, et al. Colloidal synthesis of double perovskite Cs2AgInCl6 and Mn-doped Cs2AgInCl6 nanocrystals. J Am Chem Soc. 2018;140(40):12989-12995.
52. Connor BA, Leppert L, Smith MD, Neaton JB, Karunadasa HI. Layered halide double perovskites: dimensional reduction of Cs2AgBiBr6. J Am Chem Soc. 2014;136:5235-5240.
53. Zhou L, Lin Z, Ning Z, et al. Highly efficient and stable planar perovskite solar cells with modulated diffusion passivation toward high power conversion efficiency and ultrahigh fill factor. Sol RRL. 2019;3(11):1900293.
54. Chang J, Lin Z, Zhu H, et al. Enhancing the photovoltaic performance of planar heterojunction perovskite solar cells by doping the perovskite layer with alkali metal ions. J Mater Chem A. 2016;4(42):16546-16552.
55. Ma J, Lin Z, Guo X, et al. Low-temperature solution-processed ZnO electron transport layer for highly efficient and stable planar perovskite solar cells with efficiency over 20%. Sol RRL. 2019;3(7):1900096.
56. Grancini G, Roldán-Carmona C, Zimmermann I, et al. One-year stable perovskite solar cells by 2D/3D interface engineering. Nat Commun. 2017;8:15684.
57. Ma C, Leng C, Ji Y, et al. 2D/3D perovskite hybrids as moisture-tolerant and efficient light absorbers for solar cells. Nano scale. 2016;8(43):18309-18314.
58. Bai Y, Xiao S, Hu C, et al. Dimensional engineering of a graded 3D-2D halide perovskite interface enables ultrahigh Voc enhanced stability in the p-i-n photovoltaics. Adv Energy Mater. 2017;7(20):1701038.
59. Smith IC, Hoke ET, Solis-Ibarra D, McGehee MD, Karunadasa HI. A layered hybrid perovskite solar-cell absorber with enhanced moisture stability. Angew Chem. 2014;126:11414-11417.
60. Tsai H, Nie W, Blancon J, et al. High-efficiency two-dimensional Ruddlesden-Popper perovskite solar cells. Nature. 2016;536:312-317.
61. Wang Z, Lin Q, Chmiel F, Sakai N, Herz L, Snaith H. Efficient ambient-air-stable solar cells with 2D-3D heterostructured butylammonium-caesium-formamidinium lead halide perovskites. Nat Energy. 2017;2:17135.
80. Raghavan CM, Chen TP, Li SS, et al. Low-threshold lasing from 2D homologous organic-inorganic hybrid Ruddlesden-Popper perovskite single crystals. *Nano Lett.* 2018;18(5):3221-3228.
81. Liu Y, Ye H, Zhang Y, et al. Surface-tension-controlled crystallization for high-quality 2D perovskite single crystals for ultrahigh photodetection. *Matter.* 2019;1:1-16.
82. Wang K, Wu C, Yang D, Jiang Y, Priya S. Quasi-two-dimensional halide perovskite single crystal photodetector. *ACS Nano.* 2018;12:4919-4929.
83. Zhumekenov AA, Burlakov VM, Saidaminov MI, et al. The role of surface tension in the crystallization of metal halide perovskites. *ACS Energy Lett.* 2017;2:1782-1788.
84. Frenkel J. A general theory of heterophase fluctuations and pretransition phenomena. *J Chem Phys.* 1939;7:538-547.
85. Mullin JW. *Crystallisation.* 4th ed. Oxford, UK: Butterworth Heinemann; 2001:600.
86. Liu Y, Zhang Y, Yang Z, et al. Low-temperature-gradient crystallization for multi-inch high-quality perovskite single crystals for record performance photodetectors. *Mater Today.* 2019;7(6):1584-1591.
87. Pound GM, Simnad MT, Yang L. Heterogeneous nucleation of crystals from vapor. *J Chem Phys.* 1954;22:1215-1219.
88. Wang X, Li W, Liao J, Kuan D. Recent advances in halide perovskite single-crystal thin films: fabrication methods and optoelectronic applications. *Solar RRL.* 2019;3:1800294.
89. Nernst W. Theorie der reaktionsgeschwindigkeit in heterogenen systemen. *Z Phys Chem.* 1904;47:52-55.
90. Dash JG. Clustering and percolation transitions in helium and other thin films. *Phys Rev B.* 1977;15:3136-3146.
91. Sun G, Kim JS, Kim WS, Hirasawa I, Kim WS. Modification of crystal growth mechanism of yttrium oxide in metastable solution. *J Cryst Growth.* 2002;235:529-540.
92. Bube RH. Trap-density determination by space-charge-limited currents. *J Appl Phys.* 1962;33:1733-1737.
93. Mark P, Heltrich W. Space-charge-limited currents in organic crystals. *J Appl Phys.* 1962;33:205-215.
94. Maculcan G, Sheikh A, Abdelhady A, et al. CH3NH3PbCl3 single crystals: inverse temperature crystallization and visible-blind UV-Photodetector. *J Phys Chem Lett.* 2015;6(19):3781-3786.
95. Dou L, Wong AB, Yu Y, et al. Atomically thin two-dimensional organic-inorganic hybrid perovskites. *Science.* 2015;349(6255):1518-1521.
96. Chen Z, Dong Q, Liu Y, et al. Thin single crystal perovskite solar cells to harvest below-bandgap light absorption. *Nat Commun.* 2017;8:1890.
97. Rao HS, Chen BX, Wang XD, Kuang DB, Su CY. A micron-scale laminar MAPbBr3 single crystal for an efficient and stable perovskite solar cell. *Chem Commun (Camb).* 2017;53:5163-5166.
98. Yue HL, Sun GH, Chen FC. Seeded space-limited crystallization of CH3NH3PbI3 single-crystal plates for perovskite solar cells. *Adv Electron Mater.* 2018;4:1700655.
99. Chen Z, Turedi B, Alsaloum A, et al. Single-crystal MAPbI3 perovskite solar cells exceeding 21% power conversion efficiency. *ACS Energy Lett.* 2019;4:1258-1259.
100. Huang Y, Zhang Y, Sun J, et al. The exploration of carrier behavior in the inverted mixed perovskite single-crystal solar cells. *Adv Mater Interfaces.* 2018;5(14):1800224.
101. Yang WS, Park B-W, Jung EH, et al. Iodide management in formamidinium-lead-halide-based perovskite layers for efficient solar cells. *Science.* 2017;356:1376-1379.
102. Krishna A, Gottis S, Nazeeruddin MK, Sauvage F. Mixed dimensional 2D/3D hybrid perovskite absorbers: the future of perovskite solar cells? *Adv Funct Mater.* 2019;29:1806482.
103. Stoumpos CC, Soe CMM, Tsai H, et al. High members of the 2D Ruddlesden-Popper halide perovskites: synthesis, optical properties, and solar cells of (CH3(CH2)nNH3)2(CH2NH3)3PbI16. *Chemistry.* 2017;2(3):427-440.
104. Chen YN, Sun Y, Peng JJ, et al. Tailoring organic cation of 2D air-stable organometal halide perovskites for highly efficient planar solar cells. *Adv Energy Mater.* 2017;7:1700162.
105. Yan J, Fu W, Zhang X, et al. Highly oriented two-dimensional formamidinium lead iodide perovskites with a small bandgap of 1.51 eV. *Mater Chem Front.* 2018;2:121-128.
106. Nie W, Tsai H, Asadpour R, et al. High-efficiency solution-processed perovskite solar cells with millimeter-scale grains. *Science.* 2015;347:522-525.
107. Yang S, Niu W, Wang AL, et al. Ultrathin two-organic-inorganic hybrid perovskite nanosheets with bright, tunable photoluminescence and high stability. *Angew Chem Int Ed.* 2017;56:4252-4255.
108. Liang D, Peng Y, Fu Y, et al. Color-pure violet-light-emitting diodes based on layered lead halide perovskite nanoplates. *ACS Nano.* 2016;10(7):6897-6904.
109. Tan Z, Wu Y, Hong H, et al. Two-dimensional (C4H9NH3)2PbBr4 perovskite crystals for high-performance photodetector. *J Am Chem Soc.* 2016;138(51):16612-16615.
110. Yu S, Guan X, Wong HSP. On the stochastic nature of resistive switching in metal oxide RRAM: physical modeling, monte carlo simulation, and experimental characterization. *2011 International Electron Devices Meeting.* Washington, DC: IEEE; 2011. https://doi.org/10.1109/iedm.2011.6131572.
111. Tian H, Chen H-Y, Gao B, et al. Monitoring oxygen movement by Raman spectroscopy of resistive random access memory with a graphene-inserted electrode. *Nano Lett.* 2013;13:651-657.
112. Li C, Gao B, Yao Y, et al. Direct observations of nanofilament evolution in switching processes in HfO2-based resistive random access memory by in situ TEM studies. *Adv Mater.* 2019;29:1602976.
113. Tian H, Zhao H, Wang X, et al. In situ tuning of switching window in a gate-controlled bilayer graphene-electrode resistive memory device. *Adv Mater.* 2015;27:7767-7774.
114. Lee J, Du C, Sun K, Kioupakis E, Lu WD. Tuning ionic transport in memristive devices by graphene with engineered nanopores. *ACS Nano.* 2016;10(7):3571-3579.
115. Strukov DB, Snider GS, Stewart DR, Williams RS. The missing memristor found. *Nature.* 2008;453:80-83.
116. Sangwan VK, Jariwala D, Kim IS, et al. Gate-tunable memristive phenomena mediated by grain boundaries in single-layers MoO2. *Nat Nanotechnol.* 2015;10:403-406.
117. Xie Y, Wei L, Wei G, et al. A self-powered UV photodetector based on TiO2 nanorod arrays. *Nanoscale Res Lett.* 2013;8:188.
118. Boruah BD, Misra A. Energy-efficient hydrogenated zinc oxide nanoflakes for high-performance self-powered ultraviolet photodetector. *ACS Appl Mater Interfaces.* 2016;8:18182-18188.
119. Wang K, Yang D, Wu C, Shapter J, Priya S. Mono-crystalline perovskite photovoltaics toward ultrahigh efficiency? *Joule.* 2019;3(2):311-316.
120. Li D, Cheng HC, Wang Y, et al. The effect of thermal annealing on charge transport in organolead halide perovskite
microplate field-effect transistors. Adv Mater. 2017;29:1601959.

121. Wang G, Li D, Cheng HC, et al. Wafer-scale growth of large arrays of perovskite microplate crystals for functional electronics and optoelectronics. Sci Adv. 2015;1(9):e1500613.

122. Cheng HC, Wang G, Li D, et al. Van der Waals heterojunction devices based on organohalide perovskites and two-dimensional materials. Nano Lett. 2015;16:367-373.

123. Li MK, Chen TP, Lin YF, et al. Intrinsic carrier transport of phase-pure homologous 2D organolead halide hybrid perovskite single crystals. Small. 2018;14(18):1803763.

124. Zhao L, Tian H, Silver SH, Kahn A, Ren TL, Rand BP. Ultrasensitive heterojunctions of graphene and 2D perovskites reveal spontaneous iodide loss. Joule. 2018;2:2133-2144.

125. Shen H, Li J, Wang H, et al. 2D lead-free perovskite (C\textsubscript{6}H\textsubscript{5}C\textsubscript{2}H\textsubscript{4}NH\textsubscript{3})\textsubscript{2}CsSn\textsubscript{2}I\textsubscript{7} with high hole mobility. J Phys Chem Lett. 2019;10:7-12.

126. Li J, Wang J, Zhang Y, et al. Fabrication of single phase 2D homologous perovskite microplates by mechanical exfoliation. 2D Mater. 2018;5:021001.

127. Mitzi DB, Dimitrakopoulos CD, Rosner J, Medeiros DR, Xu Z, Noyan C. Hybrid field-effect transistor based on a low-temperature melt-processed channel layer. Adv Mater. 2002;14:1772-1776.

128. Yasuda T, Fujita K, Nakashima H, Tsutsui T. Organic field-effect transistors with gate dielectric films of poly-p-xylene derivatives prepared by chemical vapor deposition. Jpn J Appl Phys. 2003;42(10 pt 1):6614-6618.

129. Mitzi DB, Chondroudis K, Kagan CR. Organic-inorganic electronics. IBM J Res Dev. 2001;45(1):29-45.

130. Dodabalapur A, Torsi L, Katz HE. Organic transistors: two-dimensional transport and improved electrical characteristics. Science. 1995;268:270-271.

131. Matsushima T, Matheret F, Heinrich B, et al. N-channel field-effect transistors with an organic-inorganic layered perovskite semiconductor. Appl Phys Lett. 2016;109:253301.

132. Matsushima T, Hwang S, Sandanayaka A, et al. Solution-processed organic-inorganic perovskite field-effect transistors with high hole mobilities. Adv Mater. 2016;28:10275-10281.

133. Yang Z, Rajagopal A, Chueh CC, et al. Stable low-bandgap Pb-Sn binary perovskites for tandem solar cells. Adv Mater. 2016;28:8990-8997.

AUTHOR BIOGRAPHIES

Jiayu Di is currently a PhD Candidate at the State Key Laboratory of Wide Band Gap Semiconductor Technology, Shaanxi Joint Key Laboratory of Graphene and Advanced Interdisciplinary Research Center for Flexible Electronics at Xidian University, under the supervision of Prof Jingjing Chang. She received her Bachelor’s degree in electronic science and technology from Tianjin University of Technology in 2018. Her research area is mainly focused on single crystal growth and device application.

Jingjing Chang received his BS degree from Sichuan University in 2010 and his PhD degree from National University of Singapore (NUS) in 2014. Since then, he worked as a research fellow in NUS, Singapore. Since 2015, he has been in Xidian University, China, where he is currently a professor in the State Key Discipline Laboratory of Wide Band Gap Semiconductor Technology in School of Microelectronics. His current research focuses on organic/metal oxide electronics, perovskite solar cells and photodetectors, flexible, and printed electronics.

Shengzhong (Frank) Liu received his PhD from Northwestern University in 1992. Upon completing his postdoctoral research at Argonne National Laboratory in 1994, he joined high-tech industrial research, most notably on solar cells with Solartronex/BP Solar and United Solar Ovonic. His current research focuses on perovskite solar cells, optoelectronic devices, single-crystalline perovskite materials, high efficiency HIT solar cells, nanoscale thin film materials and photocatalyst for photoelectrochemical water splitting. He has published more than 200 papers in peer-reviewed journals including Science, Nature, Nature Communications, Energy & Environ. Sci., Adv. Mater., Sci. Adv., Phys. Rev. X, and so forth.

How to cite this article: Di J, Chang J, Liu S(F). Recent progress of two-dimensional lead halide perovskite single crystals: Crystal growth, physical properties, and device applications. EcoMat. 2020;2:e12036. https://doi.org/10.1002/eom2.12036