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Low-Dimensional Organic–Inorganic Halide Perovskite: Structure, Properties, and Applications

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Three-dimensional (3 D) perovskite has attracted a lot of attention owing to its success in photovoltaic (PV) solar cells. However, one of its major crucial issues lies in its stability, which has limited its commercialization. An important property of organic–inorganic perovskite is the possibility of forming a layered material by using long organic cations that do not fit into the octahedral cage. These long organic cations act as a "barrier" that "caps" 3D perovskite to form the layered material. Controlling the number of perovskite layers could provide a confined structure with chemical and physical properties that are different from those of 3D perovskite. This opens up a whole new batch of interesting materials with huge potential for optoelectronic applications. This Minireview presents the synthesis, properties, and structural orientation of low-dimensional perovskite. It also discusses the progress of low-dimensional perovskite in PV solar cells, which, to date, have performance comparable to that of 3D perovskite but with enhanced stability. Finally, the use of low-dimensional perovskite in light-emitting diodes (LEDs) and photodetectors is discussed. The low-dimensional perovskites are promising candidates for LED devices, mainly because of their high radiative recombination as a result of the confined low-dimensional quantum well.

1. Introduction

Three-dimensional (3D) organic-inorganic hybrid perovskites have been one of the most intensively studied classes of materials in recent years owing to their outstanding optoelectronic properties. They emerged as leading materials in photovoltaic cells by achieving a power conversion efficiency^[1] of 22.1% in only a few years. The versatility of these materials is not only limited to photovoltaic applications but ranges to a series of optoelectronic devices such as light-emitting diodes (LEDs),^[2,3] photodetectors, transistors,^[4] and lasing applications.^[5] Threedimensional perovskite has an ABX₃ structure; it consists of a 3D network of corner-sharing MX₆ octahedra, filled with the cation "A" inside the coordinated hole. In organic-inorganic perovskite, "M" is a divalent metal cation, "X" is a halide (Cl, Br, or I), and "A" is an organic methylammonium cation that can fit into the octahedral holes. In 1986, Maruyama's group from Japan reported on a novel layered material combining organic and inorganic components that corresponded to the formula $(C_n H_{2n+1} N H_3)_2 M X_4$.^[6] This component formed a two-dimensional (2D) structure by self-assembly of the layers, which were held together by van der Waals forces and intramolecular forces. Using the nonylammonium (C₉H₁₉NH₃) salt, Maruyama's group fabricated a unique structure that was known as 2D perovskite. Goldschmidt's tolerance factor $(t)^{[7,8]}$ is a theoretical rule that uses a simple geometric consideration to predict whether the organic cation "A" will form either a 3D or 2D perovskite structure [Eq. (1)]:

$$t = \frac{R_{\rm A} + R_{\rm X}}{\sqrt{2}(R_{\rm B} + R_{\rm X})} \tag{1}$$

in which R_A , R_B , and R_x are the effective ionic radii of the corresponding ions (assuming that the individual ions are hard spheres). Calculating the values of the Goldschmidt factor predict the formation of 3D perovskite in the range of 0.8 to 1, whereas values higher than 1 predict 2D perovskite.

The present minireview provides up-to-date information on low-dimensional organic-inorganic perovskite, ranging from its synthesis and properties to a variety of optoelectronic applications. The structural aspects, synthetic approaches, and properties of 2D and quasi-2D perovskite materials are described in Section 2, and this is followed by their most-studied applications in photovoltaic solar cells in Section 3. Section 4 focuses on the use of low-dimensional perovskites in other optoelectronic applications such as LEDs and photodetection applications. An outlook regarding its future perspectives is provided in the final section. The aim of this Minireview is to provide updated and the most-relevant information regarding the properties of low-dimensional perovskite, in addition to its various applications.

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2. Synthesis and Properties of Low-Dimensional Halide Perovskite

2.1. Low dimensionally oriented organic-inorganic halide perovskite

Over the years, the self-assembly of two-dimensional organicinorganic halide perovskite has attracted a lot of attention. The ability to form an ideal 2D structure easily from an artificial quantum well is nontrivial, and it is limited upon using traditional semiconductor materials.^[9] Two-dimensional organic-inorganic halide perovskite has unique optical and physical characteristics with strongly bound exciton energy and third-order optical nonlinearity.

Motivation to find more components while retaining a sharp exciton absorbance feature led to the discovery of a new structural series of layered perovskite $(\text{RNH}_3)_2(\text{MeNH}_3)_{n-1}\text{Pb}_n|_{3n+1}$, in which n=1 corresponds to a 2D perovskite sheet, $n=\infty$ corresponds to 3D perovskite, and $2 < n < \infty$ forms a layered structure of perovskite.^[10] Layered perovskite with a bilayer and trilayer (n=2, 3) has been obtained for perovskite based on iodide, bromide, and chloride.

The structure of the layered perovskite can be determined by X-ray diffraction, which provides an important parameter, the distance between the layers. The small methylammonium cation fits into the corner-sharing octahedral cage in the PbX₆ framework (the "A" component in the ABX₃ 3D perovskite structure), whereas a bigger organic cation will not fit into this octahedral cage; therefore, it will form a layered structure. In this manner, the long organic cation will "cap" the MAX₃ perovskite, held together by van der Waals interactions, to form a layered structure. The number of layers confined in the long organic cations corresponds to "n". Different sizes of organic cations can be used to obtain a layered perovskite structure. This perovskite family consists of <001>-terminated layers, which is the one most known for oriented perovskite (Figure 1a).

The ratio between the long organic cations enables one to control the perovskite's dimensionality, whereas the type of the long organic cation can influence the crystallographic orientation of the inorganic framework. Mitzi et al.^[11] used the organic iodoformamidinium cation with Sn as the metal cation to form a series of $[NH_2C(I)NH_2]_2(CH_3NH_3)_mSn_mI_{3m+2}$ perovskite. In this family of layered perovskites, oriented perovskite sheets are separated by iodoformamidinium layers to form <110>-oriented perovskite, for which "m" corresponds to the number of sheets inside the layers. The iodine of the iodoformamidinium cation completes a 12-fold sphere coordination

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Lioz Etgar obtained his PhD 2009 from the Israel Institute of Technology (Technion) and followed by postdoctoral research with Prof. Michael Grätzel at the École polytechnique fédérale de Lausanne, Switzerland. He received a Marie Curie Fellowship and won the Wolf Prize for young scientists. Since 2012, he has been a senior lecturer at the Institute of Chemistry at the Hebrew University, at which he is an Associate Professor position since



2017. Recently, he won the Krill prize from the Wolf foundation. His research group focuses on the development of innovative solar cells. He is researching new excitonic solar-cell structures/architec-tures while designing and controlling the inorganic light-harvester structure and properties to improve the photovoltaic parameters.

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Figure 1. Oriented low-dimensional perovskite in a) <001> faces, b) <110> faces, and c) <111> faces for different numbers of layer "n", "m", and "q", respectively. Reproduced with permission from Ref. [14].

around the methylammonium cations, whereas the iodoformamidinium cations themselves form hydrogen-bonded "chains" favoring the <110>-oriented framework rather than the <001>-oriented framework, as shown in Figure 1b.

In the case of <110>- and <001>-oriented structures, if the "m" or "n" values are increased, the perovskite is transformed into a more three-dimensional structure, which progressively results in an increase in the perovskite's conductivity.

The third family of oriented 2D perovskite (Figure 1c) is less common; it corresponds to a <111>-oriented layer of the $A_2A'_{q-1}M_qX_{3q+3}$ structure, in which A' and A are organic cations.^[12,13] In this oriented 2D perovskite, the (trivalent) metal cation forms the MX_6 octahedron, and each octahedron in the outer surface contributes three halides to the termination surface. The "A" and "A" cations are interlayer and intralayer organic cations, and they can also be the same in some perovskite structures. However, unlike "n" and "m" for the <001>- and <110>-oriented perovskite families, q=1 of the <111> family results in a 0D structure and not a 1D structure, as the perovskite consists of isolated metal halide octahedra.

2.2. Synthesis of low-dimensional organic-inorganic halide perovskite

Two-dimensional layered perovskite is formed by using a solution-processed technique, whereby stoichiometric precursors are dissolved in a solution and deposited on the surface and assembled into the 2D perovskite structure. There are two main perovskite deposition techniques based on solution processes: two-step and one-step deposition. One-step deposition requires that all the precursors be dissolved in the same solution. Once the perovskite is deposited on the substrate using, for example, spin coating, slot die, or drop-casting techniques, the solvent evaporates and the perovskite crystallizes. To synthesize 3D organic–inorganic halide perovskite, a ratio of 1:1 between the metal halide and the small organic cation (which fits into the octahedral inorganic framework) is needed. However, to synthesize a pure 2D perovskite structure, a solution of metal halide and a long organic cation (which does not fit into the octahedral inorganic framework) in a 1:2 molar ratio is required. Upon mixing a metal halide with both short and long organic cations, several possibilities regarding the perovskite can occur: one, the organic cations may be locally arranged into separate structures; two, the precursors may be arranged into a more complex layered hybrid structure, in which the long organic cations separate the slabs of 3 D perovskite. The relative solubility of the long and short organic cations affects the growing structure. If the solubility of the two cations is sufficient and the precursors are in a stoichiometric ratio that corresponds to the chemical formula of layered perovskite, then the complex layer can be formed in a stable structure.^[14]

The two-step deposition method can also be used to synthesize low-dimensional perovskite. In this method, the metal halide precursor is deposited onto the substrate in the first step, whereas in the second step the metal halide electrode is dipped in a solution that contains the desired ammoniumbased cations.^[15]

Selecting the specific long organic cations (as discussed in the previous section) will lead to the growth of oriented perovskite layers of <001>, <110>, or <111>. Furthermore, changing the ratio between the organic cations influences the number of perovskite sheets inside the organic layers.

depositing 2 D-layered perovskite Upon of the $(RNH_3)_2(A)_{n-1}M_nX_{3n+1}$ structure on a substrate, the layers must be arranged in a random configuration related to the surface (i.e., perpendicular, parallel, and to certain angles). A recent study^[16] reported on a hot-casting deposition method that formed oriented perovskite layers perpendicular to the substrate. In that study, $(BA)_2(MA)_{n-1}Pb_nI_{3n+1}$ perovskite was deposited on a preheated substrate, which resulted in layered perovskite, for which the inorganic framework was perpendicular to the surface. The conductivity through this perovskite structure was better than that through a perovskite structure in which the perovskite layers were randomly oriented on the surface.



2.3. Optical and physical properties of low-dimensional halide perovskite

An important property of low-dimensional layered materials such as the hybrid perovskite is the variation in the electronic potential across the layers, which increases the exciton binding energy. The mismatch in the dielectric constant between the long organic cation (barrier, $\varepsilon_{\rm b}$) and the inorganic framework (well, $\varepsilon_{\rm w}$) determines the exciton binding energy, which is called the "dielectric confinement effect".

In the case of perovskite, the inorganic framework, PbX₄, has a high dielectric quantum well ($\varepsilon_{w} \approx 6.1$) separated by a low dielectric constant ($\varepsilon_{b} \approx 2.1$) of the alkylammonium spacer, which is considered to be the barrier.^[17] As a result of the quantum confinement and the "dielectric confinement effect", the lowdimensional organic–inorganic halide perovskite has unusually high exciton bonding energy (≈ 320 meV), along with a large oscillator strength. Therefore, by selecting different organic barriers, one can "tune" the exciton binding energy.

In addition to the exciton bonding energy, the band gap can be tuned by varying the number of perovskite layers separated by the long organic cation. Decreasing the perovskite's dimensionally results in the perovskite having a wider energy band gap. If the *n* value is varied, as in the case of perovskite from the (R-NH₃)₂(MA)_{n-1}Pb_nI_{3n+1} structure from n=1 to $n=\infty$ (e.g., 3D perovskite), the perovskite's color changes from yellow to orange, red, and dark brown, which is related to 3D perovskite.^[10, 18-21] These changes in the energy band gap are also observed in bromide-based perovskite.^[22] Another interesting feature of the perovskite's dimensionality is related to its absorbance spectra. Clear excitonic features can be observed even at room temperature in low-dimensional hybrid perovskite. As the temperature decreases, the features become clearer and exhibit a step-like structure. The step-like features are related to electron-hole free transmission and reflect the density of states.^[19,22,23]

2.4. The long organic spacers (barriers)

The density of states (DOS) in organic-inorganic perovskite shows that the conduction band maximum (CBM) is occupied mainly by the metal "M" p orbitals, whereas the valance band maximum (VBM) consists of an antibonding, fully occupied s orbital of the metal with a p orbital of the halide "X". The organic cation does not significantly contribute to the electronic states around the band edge^[24], although the band gap can be tuned by replacing the halide or the metal components.^[25-28] Although the organic cation has no direct influence around the band edge, steric hindrance or other structural effects, resulting from the organic molecules, can indirectly impact the band gap by causing structural changes in the inorganic framework.^[24,25] Given that in low-dimensional organicinorganic halide perovskite there is almost no limitation on the length or the complexity of the ammonium cation, there is a wide range of possibilities. Mitzi et al.^[25] calculated the distortion for a series of barrier molecules in (R-NH₃)₂SnI₄, 2D perovskite and their influence on the exciton binding energy and band edge.

A change in the barrier molecules results in structural distortion of the inorganic framework. The more common in-plane distortion increases the charge density of the anionic inorganic layer. In this distortion, decreases in both the valence and conduction bands' width occur. In contrast, out-of-plane distortion is less known in the perovskite structure. This distortion impacts the valence band and does not significantly affect the conduction band. Using different organic cations (barriers) enables one to tune the band gap as well as the bandwidth of the valence and conduction bands of the low-dimensional perovskite.

In addition, the barriers provide hydrophobicity to the perovskite structure (higher resistivity to humidity) more than 3D perovskite does. Several studies showed enhanced stability of 2D and quasi-2D perovskite in ambient air relative to 3D perovskite.^[18-21]

3. Low-Dimensional Halide Perovskite in Photovoltaic Solar Cells

In further discussing the interesting properties of low-dimensional perovskite, solar cells based on organic–inorganic halide perovskite can now achieve a high power conversion efficiency (PCE) of 22.1 %;^[1] however, their stability still remains a concern for large-scale manufacturing. Here, the implementation of low-dimensional halide perovskite in solar cells will be discussed. Low-dimensional perovskite has been implanted in several solar-cell structures, including planar TiO₂, mesoporous TiO₂, and TiO₂ nanorods.^[29–31] Low-dimensional perovskite solar cells exhibit better moisture resistance than their 3D counterparts.

The first report on the incorporation of low-dimensional perovskite into solar cells was reported by Smith et al.^[18] In this work, Ruddlesden–Popper layered perovskite was used in the solar cell with the phenylethylammonium (PEA) cation as the spacer for the inorganic framework, which was usually constructed of corner-sharing octahedra derived from the parent 3 D perovskite MAPbl₃.

The solar cells studied employed perovskite having the structure $(PEA)_2(MA)_{n-1}Pb_nI_{3n+1}$, for which n=3, and $(\mathsf{PEA})_2(\mathsf{MA})_2\mathsf{Pb}_3\mathsf{I}_{10}$ was used as the light harvester. The cells were fabricated in the planar structure with TiO₂ as the electron-selective layer (ETL) and 2,2',7,7'-tetrakis-[N,N-di(4-methoxyphenylamino)]-9,9'-spirobifluorine (spiro-OMeTAD) as the hole-selective layer (HTL). A maximum PCE of 7.02% and an open-circuit voltage (V_{oc}) of 1.21 V at a fast scan rate were achieved. However, a large hysteresis effect was observed owing to the sensitivity of the cells to different scan rates and to changes in the scan direction. Therefore, under steady-state conditions the cells gave a PCE of 4.73% with a V_{oc} value of 1.18 V. The stability of the 2D films was investigated by exposing them to a controlled humidity environment, and powder X-ray diffraction (PXRD) was performed several times. Over a period of 40 days, the peaks associated with Pbl₂ increased in intensity, whereas the peaks associated with the perovskite de-



creased in intensity. Furthermore, the absorbance spectra changed over time: the absorbance near the band gap of the perovskite decreased, whereas the absorbance near the band gap associated with Pbl₂ increased. With 2D perovskite there was no degradation in the PXRD patterns, and the absorption spectra did not change over a period of 46 days.

Kanatzidis et al.^[19] introduced butylammonium (BA) as the organic cation spacer; it has a solar-cell structure of mesoporous TiO₂ as the ETL and spiro-OMeTAD as the HTL, if several *n* values of n = 1, 2, 3, and 4 are synthesized from the Ruddlesden–Popper-layered perovskite structure (BA)₂(MA)_{n-1}Pb_nI_{3n+1}. Figure 2 shows the energy-band diagram of



Figure 2. Band energy diagram of $(BA)_2(MA)_{n-1}Pb_n|_{3n+1}$ perovskite for several *n* values. Reproduced with permission from Ref. [19].

 $(BA)_2(MA)_{n-1}Pb_nI_{3n+1}$ perovskite for several *n* values. The maximum efficiency approaches 4.02 % with a V_{oc} value of 0.93 V. The absorbance measurements show that if the perovskite dimensionality (low *n* values) decreases, the band gap increases owing to quantum confinement and the dielectric confinement effect.^[10,17] VBM measurements on these materials have been performed by ultraviolet photoelectron spectroscopy (UPS), which shows that if n=1 and n=2 the VBM is higher than the HOMO level of spiro-OMeTAD; therefore, it inhibits holes from being injected into spiro-OMeTAD and, thus, increases the probability of recombination in these materials.

Stability measurements have been performed on films of $(BA)_2(MA)_2Pb_3I_{10}$. The 2D and 3D films were stored at 40% humidity for 2 months without any degradation, whereas the 3D counterpart degraded into yellow PbI₂ after a short period of time, as confirmed by XRD.

Sargent et al.^[21] investigated the (PEA)₂(MA)_{*n*-1}Pb_{*n*}I_{3*n*+1} series with *n* values varying from pure 2D, that is, n = 1 (PEA)₂PbI₄, through quasi-2D cells with high *n* values, for example, n = 50, 60, and ∞ corresponding to 3D MAPbI₃ perovskite. Planar cells with a thin TiO₂ film (\approx 50 nm) as the ETL and spiro-OMeTAD (\approx 180 nm) as the HTL were used. High *n* values showed the best photovoltaic (PV) performance, whereas n =60 showed the best PCE of 15.3% with negligible hysteresis.

Optoelectronic simulations showed a decrease in mobility for low *n* values and a radiative recombination of $5 \times$ 10⁻¹⁰ cm³ s⁻¹. Using experimental values of the band gap and absorbance spectra, modeled current-voltage (J-V) curves were produced for all n values; they were compared to the experimental values (Figure 3). It was observed that upon decreasing the n value, the $V_{\rm oc}$ values of the cells increased, whereas the short-circuit current density (J_{sc}) and the fill factor (FF) values decreased. The reason for the increased $V_{\rm oc}$ value was related to slow carrier mobility for which carrier accumulation was high because of slow carrier extraction. High carrier accumulation, on the other hand, increased the radiative recombination, which resulted in low J_{sc} and FF values. Importantly, the discussion above refers to n > 6, and for n < 6, the carrier-transport properties, including diffusion length, mobility, and carrier lifetime, were poor.^[19,21,32,33] As also reported in a previous study, 2D and quasi-2D perovskite exhibited better stability than 3D perovskite.

In recent work, bromide-based 2D and quasi-2D perovskite were used in solar cells. The perovskite structure was according to the formula $(PEA)_2(MA)_{n-1}Pb_nBr_{3n+1}$, for which the halide was bromide.^[22] The different *n* values varied from pure 2D perovskite (*n* = 1) through quasi-2D perovskite (*n* > 1), and finally to 3D perovskite. High *n* values above 20 were synthesized to achieve efficient and stable cells. In contrast to previous reports, cells with and without a HTM were fabricated. Cells with *n* > 40 exhibited better PV performance than their 3D counterparts, mainly because of higher *V*_{oc} values. The band gap did not change any more if the *n* values were more than 10; however, interestingly, the *V*_{oc} value approached



Figure 3. *J*–*V* curves for different *n* values of perovskite. a) Simulation using experimental absorption spectra and band gaps and with a mobility of $0.1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. b) Simulation with a radiative recombination of $5 \times 10^{-10} \text{ cm}^3 \text{s}^{-1}$ and gradually decreasing mobility for lower *n* values. c) Experimental curves. Reproduced with permission from Ref. [21].

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higher values for quasi-2D than for 3D perovskite. A possible explanation as to why the quasi-2D cells had better V_{oc} values than the 3D cells was related to low carrier mobility, as discussed above, which enhanced the V_{oc} value. Moreover, density functional theory (DFT) calculations showed that if the perovskite dimensionality increased, the electrical conductivity also increased.

Mohite et al.^[16] showed that the crystalline structure of the $(BA)_2(MA)_{n-1}Pb_n l_{3n+1}$ series for n=4 $(BA)_2(MA)_3Pb_4 l_{13}$ improved by using the hot-casting one-step deposition technique. In that report, the spin-coating process was performed on preheated substrates that varied from room temperature to 150 °C. The films that were deposited using the hot-casting method exhibited bigger grain sizes than the average size in the case of one-step deposition, and more compact and uniform coverage was evident in the atomic force microscopy (AFM) and scanning electron microscopy (SEM) images. A comparison of the full-width at half-maximum (FWHM) made by grazing-incidence XRD (GIXRD) of the (202) crystallographic plane for the different casting temperatures suggested that casting temperatures above 110 °C resulted in better crystallinity.

Moreover, grazing-incidence wide-angle X-ray scattering (GIWAXS) analysis at room temperature revealed a random grain orientation within the polycrystalline film, whereas in the case of the hot-casting films, the orientation favored the (101) crystallographic plan, which suggested that the inorganic framework was vertical to the substrate. Solar cells employing (BA)₂(MA)₃Pb₄I₁₃ (n=4) as the light absorber in a planar structure with [6,6]-phenyl C₆₁ butyric acid methyl ester (PCBM) as the ETL and poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) as the HTL were fabricated. A PCE of 12.51% along with a V_{oc} value of 1.01 V by using the hot-casting deposition were achieved.

The PV performance of the hot-casted solar cells showed an improvement over those cells made at room-temperature deposition. The hot-casting deposition technique formed well-oriented perovskite layers, in which the inorganic framework was vertical to the substrate, and this allowed pathways for better charge transport through the perovskite film towards the contacts. Stability measurements showed better reliability for the 2D-based cells both in the case of light stress and humidity over their 3D counterparts. The cells did not exhibit sensitivity to scan speed or scan direction and were hysteresis free.

The presence of lead in most organic–inorganic halide perovskite based PV devices is a major concern for communities as a result of environmental toxicity and stringent disposal laws. Recent work by Liao et al. showed low dimensionality as a promising alternative to achieve high stability in lead-free perovskite solar cells.^[34] Tin (Sn)-based quasi-2D-perovskite with formamidinium (FA) and phenylethylammonium cations has been demonstrated. The resulting perovskite of the formula (PEA)₂(FA)_{*n*-1}Sn_{*n*}l_{3*n*+1} has been used for the fabrication of cells that show PCE values up to 5.94%. Interestingly, un-encapsulated devices were found to be stable up to 100 h, and no degradation in the performance was noticed.

4. Low-Dimensional Halide Perovskite in Optoelectronic Applications

4.1. Low-dimensional perovskite in LEDs

The most extensively studied application of halide perovskites, after extensive work in photovoltaics, is their application in light-emitting diodes (LEDs). In fact, their use in LEDs was first reported in the 1990s, even before the advent of photovoltaic systems.[35-37] The initial reports on perovskite-based LEDs were unable to attract the attention of the scientific community because of the poor performance of these devices and their marked low stability, as they only worked at cryogenic temperatures. Era et al.^[36] reported on 2D-layered perovskite-based quantum-well structures with the use of phenylethylammonium lead iodide (C₆H₅C₂H₄NH₃)₂PbI₄. They succeeded in fabricating electroluminescent (EL) devices with this material and operated them at cryogenic temperatures. Recently, after achieving a power conversion efficiency of more than 22% for perovskite-based solar cells, the research community has again focused on perovskite-based LEDs with the use of normal 3D perovskite to fabricate quantum-confined 2D-layered perovskite. The poor performance of methylammonium lead iodide MAPbl₃-based perovskite in LED applications can be attributed to low exciton binding energies in the range of 9 to 60 meV^[38,39] which result in free charge carriers and, hence, predominantly nonradiative recombination.

Li and co-workers successfully demonstrated the use of phenylmethanamine lead iodide $(C_6H_5CH_2)_2PbI_4$ (as shown in Figure 4a.), a 2D perovskite-based green LED, working at room temperature.^[40] The authors investigated the stability of the device under 50% relative humidity conditions and found no degradation in the XRD pattern for 5 days, as seen in Figure 4b. The absorption and photoluminescence spectra of thin films of the material are presented in Figure 4c.

The first band in the absorption spectrum is attributed to high-order exciton transition energy levels and to charge-transfer transition between the organic and inorganic layers, whereas the second band is attributed to the intrinsic exciton absorption of the formed quantum-well structures.

Figure 4d shows the transient photoluminescence (PL) decay of the 2D perovskite film; the average PL lifetime was calculated to be approximately 37 ps by using a double exponential decay function, which was correlated with the strong exciton–phonon interaction in 2D perovskite at room temperature.^[41,42] The LED devices fabricated with this material exhibited an electroluminescence (EL) band at $\lambda = 526$ nm along with a narrow FWHM; the results were in agreement with those obtained by PL spectroscopy, which indicated its origin from excitonic emission of 2D perovskite. The device exhibited 9 cd m⁻² luminance under a driving voltage of 5 V and a starting voltage of 2.8 V. The device's stability was poor, as it exhibited a lifetime of less than 1 min.

Yuan et al.^[43] reported on a series of quantum-sized tuned grains of quasi-2D-mixed perovskite material that had overcome the issue of undesired nonradiative recombination. The quasi-2D perovskite material studied was synthesized by using



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Figure 4. a) Chemical structure of the $(C_6H_5CH_2NH_3)_2PbI_4$ layered perovskite. b) X-ray diffraction profiles of a $(C_6H_5CH_2NH_3)_2PbI_4$ film on a glass substrate. Blue and red lines show the data before and after exposure to an atmospheric environment of $\approx 50\%$ relative humidity for 5 days, respectively. c) Absorption and photoluminescence spectra of a $(C_6H_5CH_2NH_3)_2PbI_4$ perovskite film spin coated on a glass substrate. d) Femtosecond PL decay trace of a $(C_6H_5CH_2NH_3)_2PbI_4$ perovskite film spin coated on a glass substrate. Reproduced with permission from Ref. [40].

phenylethylammonium (C₆H₅C₂H₄NH₃) as a spacer. The device's EL and photoluminescence quantum yield (PL-QY) were tuned by varying the n values and the number of PbI_4 layers in the quasi-2D perovskite. It was found that significantly higher values of PL-QY, for example, 10.1 and 10.6%, were achieved for quasi-2D-layered materials with n=3, and n=5, respectively, as compared with a PL-QY of less than 0.1% for n = 1 under the same excitation intensity of 6 mW cm⁻². The devices fabricated with an indium tin oxide (ITO)/thin TiO₂/ $(PEA)_2(MA)_{n-1}PbnI_{3n+1}/poly(9,9'-octylfluorence)$ F8/MoO₃/Au structure performed well and achieved an external quantum efficiency (EQE) of 8.8% and 80 W sr⁻¹m⁻² radiance in the nearinfrared (NIR) region.

Liang et al.^[44] utilized quantum-confined 2D perovskite based on 2-phenylethylammonium lead bromide (PEA-PbBr₄) to realize color-pure violet LEDs. The material was found to assemble in well-confined quantum-well structures with an energy diagram shown in Figure 5 a, b and with a repeating dielectric spacer layer, sandwiching 3D PbBr₆ octahedra in between. The better-performing high-quality perovskite layer with a millimeter grain size was achieved through a solvent-annealing procedure in the presence of DMF vapors.

The 2D materials exhibited entirely different morphology and topographical behavior upon utilizing direct-baking and solvent-annealing methods, as determined by AFM and SEM. The films deposited through the direct baking of perovskite were smoother than those deposited by using solvent annealing in the presence of DMF, which in turn, was found to drasti-



Figure 5. a) Crystal structure of 2-phenylethylammonium lead bromide, $(PEA)_2PbBr_4$, which is a 2D-layered perovskite. The inorganic layers consist of corner-sharing lead bromide octahedra, within which the green and orange balls represent Pb and Br atoms, respectively. The organic layers consist of PEA cations. The gray balls represent carbon atoms, the white balls represent hydrogen atoms, and the blue balls represent nitrogen atoms. b) Schematic energy diagram showing multiple quantum wells in layered (PEA)₂PbBr₄. Reproduced with permission from Ref. [44].



cally affect the performance of the devices. The absorption and PL spectra of the grown thin film (by direct baking) and the nanoplates (using solvent annealing) showed a strong absorption band at $\lambda = 404$ nm and an intense PL band at $\lambda =$ 407 nm, which were attributed to the high PL-QY values of the films, from 10% for the thin film to 26% for the nanoplates. The PL lifetimes of both films were studied with the help of wavelength-resolved time-correlated single photon counting, and the PL lifetime was approximately two times longer (1.27 vs. 0.62 ns) in the nanoplates.

The cross-section SEM of the fabricated LED devices and the energy-level diagram of the different layers are shown in Figure 6a, b. The PL and EL spectra of the devices are both shown in Figure 6c, and the PL maximum is blue-shifted by 3 nm relative to the EL maximum; this was attributed to minor optical cavity effects. Figure 6d presents the current density-voltage curves of the LED devices. As can be seen in the figure, the EQE of the devices with nanoplates is approximately 20 times higher than that of the devices fabricated with thin films, that is, 0.04 versus 0.002%. The low EQE for the pure-violet LED is comparable to that of similar LEDs formed with other materials, such as Cds/ZnS core-shell quantum dots.^[45]

Hu et al.^[46] recently reported on tunable LEDs with fine emission and different color regions by using the 2D perovskite structure (the *n* values were in the range of n=1 to n=6) achieved through butylammonium iodide (C₄H₉NH₃I) as a spacer. The high-quality films deposited through the fast-deposition process were characterized by XRD, AFM, absorption spectroscopy, and PL. The authors correlated the presence of an intense absorption band at approximately $\lambda = 510$ nm with a strong photon–exciton interaction confined within the 2D quantum wells, which resulted in a long lifetime and a large exciton binding energy of 300 meV.^[47] The large exciton binding energy, as supported by the PL spectra of the films, is a condition that favors radiative recombination.

Hoke et al.^[48] demonstrated a stable red LED in contrast to previous reports, which reported some difficulties in achieving a stable red LED owing to phase separation of the iodide/bromide counterparts. A maximum luminance of 214 cd m⁻² was achieved at 8 V, whereas the maximum EQE was 2.29%. Furthermore, this was a seminal report demonstrating differently colored LEDs by varying halide ions in 2D perovskite.

Table 1 summarizes LEDs having different architectures that were fabricated by using 2D perovskite at various emission wavelengths.

4.2. Low-dimensional halide perovskite in photodetectors

Another possible application using 2D perovskite is with photodetectors. Li et al.^[49] reported on high-performance photodetectors based on 2D nanosheets of MAPbl₃. The extremely thin nanosheets, having a thickness of approximately 20 nm, were achieved through the chemical vapor deposition (CVD) method on Pbl₂ crystals already deposited on top of SiO₂



Figure 6. a) Cross-sectional SEM image of the (PEA)₂PbBr₄ LED device. The scale bar is 200 nm. b) Energy-level diagram for the (PEA)₂PbBr₄ LED device. The valence band edge of (PEA)₂PbBr₄ was measured by UPS, and the conduction band edge was calculated from the optical gap; other values were taken from references. c) Normalized luminescence of a typical LED device based on (PEA)₂PbBr₄ nanoplates obtained from DMF vapor annealing operating at 6 V. The EL and PL bands are located at $\lambda = 410$ and 407 nm, respectively. The weak EL band at $\lambda = 375$ nm is from 1,3,5-tris(1-phenyl-1*H*-benzimidazole-2-yl)benzene (TPBi), consistent with its PL spectrum (gray curve). The inset shows a picture of uniform violet light emission from a (PEA)₂PbBr₄ LED device. d) Current–voltage (*J–V*) dependence (red symbols) and EQEs (blue symbols) for LEDs fabricated with a (PEA)₂PbBr₄ thin film (open symbols) and nanoplates (solid symbols). Reproduced with permission from Ref. [44].

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Color	Device architecture including perovskite type	λ_{\max} of EL [nm]	V _{on} [V]	Max. EQE [%]	Ref.
green	ITO/PEDOT:PSS/(C ₆ H ₅ CH ₂ NH ₃) ₂ PbI ₄ /Bphen/Al	526	2.8	0.005	[37]
red	ITO/TiO ₂ /(PEA) ₂ (MA) _{n-1} Pb _n I _{3n+1} /F8/MoO ₃ /Au	735 $(n=3)$ 755 $(n=5)$ 760 $(n=10)$ 770 $(n=40)$	3.8	8.8	[40]
violet	ITO/PEDOT:PSS/(PEA) ₂ PbBr ₄ /TPBi/Ca/Al	410	2.5	0.04	[41]
red	ITO/PEDOT:PSS/poly-TPD/(BA) ₂ (MA) ₂ Pb ₃ I ₁₀ /TPBi/LiF/AI	700	2.7	2.29	[43]
green	ITO/PEDOT:PSS/poly-TPD/(BA) ₂ (MA) ₄ Pb ₅ Br ₁₆ /TPBi/LiF/Al	523	3.3	1.01	[43]
blue	ITO/PEDOT:PSS/poly-TPD/(BA) ₂ (MA) ₂ Pb ₃ Br ₇ Cl ₃ /TPBi/LiF/Al	468	5.2	0.01	[43]
red	ITO/poly-TPD/BAI:MAPbl ₃ /TPBi/LiF/AI	748	5-6.5	10.4	[50]
green	ITO/poly-TPD/BABr:MAPbBr ₃ /TPBi/LiF/Al	513	5-6.5	9.3	[50]
red	ITO/ZnO:PEIE/ NFPI ₇ /TFB/MoO _x /Au	786	2.3	9.6	[51]
red	ITO/ZnO:PEIE/NFPI ₆ B/TFB/MoO,/Au	763	2.6	11.7	[51]
green	ITO/PEDOT:PSS/(PEA) ₂ (MA) _{n-1} Pb _n Br _{3/n+1} /TPBi/LiF/AI	520 and 526 for <i>n</i> = 3 and 5	-	7.4	[52]

 $phenyl)-N, N'-bis(phenyl) benzidine]; \ \ PEIE = polyethylenimine; \ \ TFB = poly[9,9-dioctylfluorene-co-N-(4-butylphenyl)diphenylamine].$

sheets to achieve planar devices, whereas if ITO was used as the substrate, it was possible to fabricate vertical devices. The substrate preparation step involved sequential photoetching of ITO followed by O_2 plasma etching and removal of photoresist; then, the perovskite layer was deposited on these substrates by using a two-step method followed by counter electrode evaporation to complete the photodetector device.

The photo response was higher for the vertical device than for the planar device. The highest responsivity of 36 mAW⁻¹ was achieved at an excitation power rate of 50.82 μ W owing to the low trap density and the short carrier diffusion length in 2D perovskite.

5. Summary and Outlook

This Minireview was divided into three main parts: the structure and properties of 2D perovskite, the use of this family of materials in photovoltaic cells, and their recent use in other optoelectronic applications. This Minireview enables one to get an idea of the potential of this family of materials and their use in the past as well as the most up-to-date news regarding their use in photovoltaic and optoelectronic applications.

Two-dimensional perovskite has been well known for many years. However, owing to the remarkable power conversion efficiency of 3D perovskite, 2D perovskite has been studied less because of the breakthrough of its counterparts. This paper discussed the significance of the long organic cation and its effect on the structure, as well as the optical and physical properties of 2D perovskite, which also now influence those applications that can be implemented by using these materials.

The possibility of synthesizing 2D perovskite by using various organic barriers opens up a whole new batch of interesting materials with huge potential for optoelectronic applications. This potential is more pronounced for 2D perovskites than for their 3D perovskite counterparts, as the 3D structure is limited by the possible elements that can be changed in the perovskite structure, such as the metal, the halide, and the small organic cation (usually methylammonium is used). On the other hand, 2D perovskite, as discussed above in this Minireview, can use organic barriers with different chain lengths, aromatic rings, and double bonds, amongst other structures, which results in different optical, structural, and electronic properties.

Moreover, 2D perovskite was recently shown to exhibit efficiencies similar to those of 3D perovskite in solar cells, for which the big advantage was related to its better stability relative to that of 3D perovskite. Stability is a crucial issue, and therefore, designing stable perovskite while maintaining or improving its properties is a big future step needed for commercializing these materials in the photovoltaic field. Taking advantage of their properties, 2D perovskites are also promising candidates for light-emitting diode devices, mainly because of their high radiative recombination resulting from the confined 2D quantum well.

Two-dimensional and quasi-two-dimensional perovskites are an important and interesting family of materials with still many unknown properties in terms of their crystallographic structure, optical transitions, and electronic properties. Moreover, 2D perovskite requires only simple and easy processing methods, which is one of the major reasons for the attractiveness of 3D perovskite. Thus, 2D perovskite materials are excellent candidates for stable perovskite that can be used for high-efficiency solar cells and optoelectronic applications.

Conflict of interest

The authors declare no conflict of interest.

Keywords: exciton binding energy · layered compounds · optoelectronics · perovskite phases · solar cells



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