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Low dimensional organic-inorganic halide perovskite: structure, properties, and applications

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Abstract

Three-dimensional (3D) perovskite has attracted a lot of attention due to its success in photovoltaic (PV) solar cells. However, one the 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 using long organic cations that do not fit into the octahedra cage. The long organic cation acts as a “barrier” that “caps” the 3D perovskite forming the layered material. Controlling the number of perovskite layers could provide a confined structure with different chemical and physical properties than 3D perovskite has. This opens up a whole new batch of interesting materials with huge potential for optoelectronic applications. This mini review 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 a comparable performance but with enhanced stability in comparison with the 3D perovskite. Finally, the use of low-dimensional perovskite in LEDs and photodetectors is discussed. The low-dimensional perovskites are promising candidates for LED devices, mainly due to 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 class of materials in recent years owing to their outstanding optoelectronic properties. They emerged as a leading material in photovoltaic cells by achieving a 22.1% power conversion efficiency 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), photodetectors, transistors, and lasing applications.

The 3D perovskite has the structure ABX₃; 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 methyl...
ammonium cation that can fit into the octahedral holes. In 1986 Yusei Maruyama's group from Japan reported on a novel layered material combining organic and inorganic components that correspond to the formula \((\text{C}_n\text{H}_2n+1\text{NH}_3)_2\text{MX}_4\). This component forms a two-dimensional (2D) structure by self-assembly of the layers, which are held together by van der Walls and intramolecular forces. Using the salt of octylammonium- \(\text{C}_9\text{H}_{19}\text{NH}_3\), Maruyama's group fabricated a unique structure that was known as 2D perovskite. Goldschmidt’s tolerance factor\(^7,8\) is a theoretical rule, using a simple geometric consideration, to predict whether the organic cation 'A' will form either a 3D or 2D perovskite structure: 

\[
t = \frac{R_A + R_X}{\sqrt{2(R_B + R_X)}},
\]

where \(R_A, R_B\) 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 0.8-1, whereas values higher than 1 predict 2D perovskite.

The present mini review provides up-to-date information on low dimensional organic-inorganic perovskite, ranging from its synthesis and properties to the variety of optoelectronic applications. The structural aspects, synthetic approaches, and properties of 2D and quasi-2D perovskite materials are described in section 2, 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 photo-detection applications. An outlook regarding its future perspective is provided in the final section. The aim of the mini review is to provide updated and the most relevant information regarding the properties and variety of applications available for low-dimensional perovskite.

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 organic-inorganic halide perovskite has attracted a lot of attention. The ability to easily form an ideal 2D structure from an artificial quantum well is non-trivial, and it is limited when using traditional semiconductor materials.\(^9\) The 2D organic inorganic halide perovskite has unique optical and physical characteristics with strongly bound exciton energy and third-order optical nonlinearity.

The motivation to find more components while retaining the sharp exciton absorbance feature led to the discovery of a new structural series of layered perovskite \((\text{RNH}_3)_2(\text{MeNH}_3)_{n-1}\text{Pb}_n\text{I}_{3n+1}\), where \(n=1\) corresponds to a 2D perovskite sheet, \(n=\infty\) corresponds to 3D perovskite,
and 2<n<∞ forms a layered structure of perovskite\textsuperscript{10}. Layered perovskite with a bilayer and tri-layer (n=2,3) was 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 PbX\textsubscript{6} framework (the 'A' component in the ABX\textsubscript{3} 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 MAX\textsubscript{3} perovskite, held together by van der Waals interactions, forming 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.\textsuperscript{11} used the organic cation iodoformamidinium with Sn as the metal cation, to form a series of [NH\textsubscript{2}C(I)NH\textsubscript{2}]\textsubscript{2}(CH\textsubscript{3}NH\textsubscript{3})\textsubscript{m}Sn\textsubscript{m+2} perovskite.

In this family of layered perovskites oriented perovskite sheets are separated by iodoformamidinium layers forming <110>-oriented perovskite, where ‘m’ corresponds to the number of sheets inside the layers. The iodine of the iodoformamidinium cation completes a 12-fold sphere coordination around the methyl ammonium cations, whereas the iodoformamidinium cations themselves form hydrogen-bonded “chains” favoring the <110>-oriented rather than the <001>-oriented framework, as shown in Figure 1B.

In the case of <110> and <001>-oriented structures, when the ‘m’ or ‘n’ values are increased, the perovskite is transformed to be more three-dimensional, which progressively results in increasing 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 structure A\textsubscript{2}A\textsuperscript{'}\textsubscript{q}M\textsubscript{q}X\textsubscript{3q+3}, where A’ and A are organic cations\textsuperscript{12,13}. In this oriented 2D perovskite the (trivalent) metal cation forms the MX\textsubscript{6} octahedron and each octahedron in the outer surface contributes three halides to the termination surface. The cations ‘A’ and ‘A’ are interlayer and intralayer organic cations, and 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 an 0D structure and not 1D, since the perovskite consists of isolated metal halide octahedra.
2.2 Synthesis of low-dimensional organic inorganic halide perovskite

The 2D layered perovskite is formed 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 the solution processed: two-step and one-step deposition. The one-step deposition requires that all the precursors will be dissolved in the same solution. Once the perovskite has been deposited on the substrate using, for example, spin coating, slot die, or drop-casting techniques, the solvent evaporates and the perovskite crystallizes. In order to synthesize 3D organic inorganic halide perovskite, a ratio of 1:1 between the metal halide and the small organic cation (which fits the octahedral inorganic framework) is needed. However, in order to synthesize a pure 2D perovskite structure, a solution of metal halide and a long organic cation (which does not fit the octahedral inorganic framework) in a 1:2 molar ratio is required. When metal halide is mixed with both short and long organic cations, several possibilities regarding the perovskite could occur:

(a) The organic cations may be locally arranged into separate structures, (b) the precursors may be arranged into a more complex layered hybrid structure in which the long organic cations separate the slabs of the 3D perovskite. The relative solubility of the long and short organic cations affects the growing structure. When 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.\textsuperscript{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 ammonium-based cations. 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.

When depositing 2D-layered perovskite of the structure (RNH₃)_2(A)_{n−1}M_nX_{3n+1} 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 reported on a hot casting deposition method that forms oriented perovskite layers perpendicular to the substrate. In this study (BA)₂(MA)_{n−1}Pb_nI_{3n+1} perovskite was deposited on pre-heated substrate, which results in layered perovskite where the inorganic framework is perpendicular to the surface. This enables better conductivity through the perovskite structure compared with the case of a random orientation of the perovskite layers 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, \( \varepsilon_b \)) and the inorganic framework (well, \( \varepsilon_w \)) 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. As a result of the quantum confinement and the “dielectric confinement effect”, the low-dimensional organic inorganic halide perovskite has unusually high exciton bonding energy (~320meV), 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. When the n value is varied, as in the case of perovskite from the structure (R-NH₃)₂(MA)_{n−1}Pb_nI_{3n+1} from n=1 to n=∞ (e.g., 3D perovskite), the perovskite’s color changes from yellow to orange, red, and dark brown, which is related to 3D perovskite. These changes in the energy band gap were also observed in bromide-based perovskite. 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-dimension hybrid perovskite. As the temperature decreases, the features become clearer and exhibit a step-like structure. The step-like features are related to the electron-hole free transmission and reflect the density of states.\textsuperscript{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 antibonding of a 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\textsuperscript{24}, although the band gap can be tuned by replacing the halide or the metal components.\textsuperscript{25,26,27,28} 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.\textsuperscript{24,25} Since in low-dimensional organic-inorganic 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.\textsuperscript{25} calculated the distortion for a series of barrier molecules in (R-NH\textsubscript{3})\textsubscript{2}SnI\textsubscript{4}, 2D perovskite and their influence on the exciton binding energy and band edge. Changing 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, decrement of both the valence and conduction bands’ width occurs. 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 (a higher resistivity to humidity) more than the 3D perovskite does. Several studies showed enhanced stability of 2D and quasi-2D perovskite in ambient air compared with 3D perovskite.\textsuperscript{18,19,20,21}

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\%; 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 was implanted in several solar cell structures including planar TiO$_2$, mesoporous TiO$_2$, and TiO$_2$ nanorods. The low-dimensional perovskite solar cells exhibit better moisture resistance than do their 3D counterparts. The first report on the incorporation of low-dimension perovskite into solar cells was reported by Smith et al. In this work, Ruddlesden-Popper layered perovskite was used in the solar cell with phenylethylammonium (PEA) cation as the spacer for the inorganic framework, which is usually constructed of corner-sharing ocahedra that is derived from the parent 3D perovskite MAPbI$_3$. The solar cells studied employed perovskite having the structure (PEA)$_2$(MA)$_{n-1}$Pb$_n$I$_{3n+1}$ where $n=3$, ((PEA)$_2$(MA)$_2$PbI$_6$) was used as the light harvester. The cells were fabricated in the planar structure with TiO$_2$ as the electron selective layer (ETL) and spiro-OmeTAD as the hole selective layer (HTL). A maximum PCE of 7.02% and a $V_{oc}$ value of 1.21V using a fast scan rate were achieved. However, a large hysteresis effect was observed, due to the sensitivity of the cells to different scan rates and to the changes in the scan direction. Therefore, when the cells were measured under steady state conditions, a PCE of 4.73% with a $V_{oc}$ value of 1.18V was observed. 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 PbI$_2$ increased in intensity, whereas the peaks associated with the perovskite decreased in intensity. Furthermore, the absorbance spectra changed over time, since the absorbance near the band gap of the perovskite decreases, whereas the absorbance near the band gap associated with PbI$_2$ increases. With 2D perovskite there is no degradation in the PXRD patterns and the absorption spectra did not change over a period of 46 days.

Kanatzidis et al. introduced butylammonium (BA) as the organic cation spacer; it has a solar cell structure of mesoporous TiO$_2$ as the ETL and spiro-OmeTAD as the HTL, when several $n$ values of $n=1,2,3,4$ are synthesized from the Ruddlesden-Popper layered perovskite structure (BA)$_2$(MA)$_{n}$Pb$_n$I$_{3n+1}$. Figure 2 shows the energy band diagram of (BA)$_2$(MA)$_{n}$Pb$_n$I$_{3n+1}$ perovskite for several $n$ values. The maximum efficiency approached 4.02% with a $V_{oc}$ value of 0.93 V. The absorbance measurements showed that when the perovskite dimensionality (low $n$ values) decreases, the band gap increases, owing to the quantum confinement and the dielectric confinement effect. VBM measurements on these materials have been carried out by Ultraviolet photoelectron spectroscopy (UPS), which show that when $n=1$ and $n=2$ the VBM is higher than the HOMO level of the spiro-OMETAD; therefore, it inhibits holes from...
being injected into the spiro-OMETAD and thus increases the probability of recombination in these materials.

Figure 2: Band energy diagram of (BA)$_2$(MA)$_n$Pb$_3$I$_{3n+1}$ perovskite for several n values. Reproduced with permission from reference 19.

Stability measurements have been carried out on films of (BA)$_2$(MA)$_2$Pb$_3$I$_{10}$. The 2D and 3D films were stored at 40% humidity for 2 months without any degradation, whereas the 3D counterpart degraded into yellow PbI$_2$ after a short period of time, as confirmed by XRD. Sargent et al.$^{21}$ investigated the (PEA)$_2$(MA)$_{n-1}$Pb$_3$I$_{3n+1}$ series with n values varying from pure 2D, i.e., n=1 (PEA)$_2$PbI$_4$ through quasi-2D cells with high n values e.g., n=50, 60 and n=infinty corresponding to 3D MAPbI$_3$ perovskite. Planar cells with thin TiO$_2$ film (~50nm) as the ETL and spiro-OMETAD (~180nm) as the HTL were used. High n values showed the best 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 $5\times10^{-10}$ cm$^3$ s$^{-1}$. Using experimental values of band gap and absorbance spectra, modeled J-V curves were produced for all n values; they were compared to the experimental values (Figure 3). It was observed that when the n values decrease, the $V_{oc}$ values of the cells increase, whereas the $J_{sc}$ and FF values decrease. The reason for the increased $V_{oc}$ value is related to the slow carrier mobility, where the carrier accumulation is high, due to slow carrier extraction. High carrier accumulation, on the other hand, increases the radiative recombination, which results in low $J_{sc}$ and FF values. Importantly, the discussion above refers to n>6, where for n<6 the carrier transport properties including diffusion length, mobility, and
carrier life time are poor.\textsuperscript{19,21,32,33} As reported also in the previous study, the 2D and quasi-2D perovksite exhibited better stability than did the 3D perovskite.

![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 cm\(^2\) V\(^{-1}\) s\(^{-1}\). (b) Simulation with a radiative recombination of \(5 \times 10^{-10}\) cm\(^3\) s\(^{-1}\) and gradually decreasing mobility for lower n values. (c) Experimental curves. Reproduced with permission from ref. 21](image)

In a recent work, bromide-based 2D and quasi-2D perovskite were used in the solar cell. The perovskite structure was according to the formula \((\text{PEA})_2(\text{MA})_{n-1}\text{Pb}_n\text{Br}_{3n+1}\), where the halide was bromide.\textsuperscript{22} The different n values varied from pure 2D perovskite \((n=1)\) through quasi-2D perovskite \((n>1)\) and 3D perovskite. High n values above 20 were synthesized in order to achieve efficient and stable cells. In contrast to previous reports, cells with and without HTM were fabricated. Cells with \(n>40\) exhibited better PV performance than did their 3D counterpart, mainly due to a higher \(V_{oc}\) value. The band gap does not change any more when the n values are more than 10; however, interestingly, \(V_{oc}\) value approached higher values for quasi-2D compared with 3D perovskite. A possible explanation for the better \(V_{oc}\) value of quasi-2D cells compared with 3D cells is related to the low carrier mobility, as discussed above, which enhances the \(V_{oc}\) value. Moreover, density functional theory (DFT) calculations show that when the perovskite dimensionality increases, the electrical conductivity also increases. Mohite et al.\textsuperscript{16} showed that the crystalline structure of the \((\text{BA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}\) series for \(n=4\) \((\text{BA})_2(\text{MA})_3\text{Pb}_4\text{I}_{13}\) improved by using the hot-casting one-step deposition technique. In this report the spin-coating process was carried out on pre-heated substrates that vary from room temperature to 150\(^{\circ}\)C. The films that were deposited using the hot-casting method exhibit 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 SEM images. The comparison of the full-width at half-maximum (FWHM) made by Graded XRD (GIXRD)
of the (202) crystallographic plan for the different casting temperatures suggests that casting temperatures above 110°C result in better crystallinity.

Moreover, GIWAX analysis at room temperature revealed a random grain orientation within the poly crystalline film, whereas in the case of the hot-casting films, the orientation favored the (101) crystallographic plan, which suggests that the inorganic framework is vertical to the substrate. Solar cells employing \((BA)_2(\text{MA})_3\text{Pb}_4\text{I}_{13} \) as the light absorber in a planar structure using PCBM as the ETL and PEDOT:PSS as the HTL were fabricated. A PCE of 12.51% along with a \(V_{oc}\) value of 1.01V using the hot-casting deposition was 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 forms well-oriented perovskite layers in which the inorganic framework is vertical to the substrate, allowing pathways for better charge transport through the perovskite film towards the contacts. Stability measurements show better reliability for the 2D-based cells both in the case of light stress and humidity over their 3D counterparts. The cells do not exhibit sensitivity to scan speed or scan direction and are hysteresis free.

The presence of lead in most of the organic-inorganic halide perovskite based PV devices is one of the major concerns towards the community, due to its environmental toxicity and stringent disposal laws. Recent work by Y. Liao et al. showed the low dimensionality as a promising alternative in order to achieve higher stability in lead free perovskite solar cells.\(^{34}\)

Tin (Sn) based quasi 2D-perovskite with formamidinium (FA) and phenylethylammonium cations was demonstrated. The resulting perovskite of the formula \((\text{PEA})_2(\text{FA})_{n-1}\text{Sn}_n\text{I}_{3n+1}\) has been used for the cell fabrication, showing PCE up to 5.94%. Interestingly, the unencapsulated devices were found stable up to 100 hours and no degradation in the performance has been 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.\(^{35,36,37}\) 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 the marked low stability, since they only worked at cryogenic temperatures. M. Era et al.\(^{36}\) reported on the 2D-layered
perovskite-based quantum well structures using phenylethylammonium lead iodide (C₆H₅C₂H₄NH₃)₂PbI₄. They succeeded in fabricating the Electro-luminescent (EL) devices with this material, and operated them at cryogenic temperatures. Recently, after achieving more than 22% power conversion efficiency of perovskite-based solar cells, the research community focused again on perovskite-based LEDs, using normal 3D perovskites to fabricate quantum-confined 2D-layered perovskite. The poor performance of methylammonium lead iodide MAPbI₃-based perovskite in LED applications can be attributed to the low exciton binding energies in the range of 9 to 60 meV, resulting in free charge carriers, and hence, a predominantly non-radiative recombination.

R. Li and co-workers successfully demonstrated the use of phenylmethanamine lead iodide (C₆H₅CH₂)₂PbI₄ (as shown in Figure 4a.), 2D perovskite-based green LED, working at room temperature. The authors investigated the stability of the device under 50% relative humidity conditions, and found no degradation in the XRD pattern for five days, as can be 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 spectra is attributed to the high-order exciton transition energy levels and to the charge transfer transition between 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 PL decay of the 2D perovskite film; the average PL lifetime was calculated to be about 37 ps by using the double exponential decay function, which was correlated with the strong exciton-phonon interaction in 2D perovskite at room temperature. The LED devices fabricated with this material exhibited an electro luminescence (EL) peak at 526 nm along with a narrow FWHM, and were in agreement with the PL spectrum, indicating its origin from an excitonic emission of the 2D perovskite. The device exhibited 9 cd/m² luminance under a driving voltage of 5V and a starting voltage of 2.8 V. The device’s stability was poor, since it exhibited less than 1 minute lifetime.
Figure 4: (a) Chemical structure of the (C₆H₅CH₂NH₃)₂PbI₄ layered perovskite. (b) X-ray diffraction profiles of a (C₆H₅CH₂NH₃)₂PbI₄ film on a glass substrate. Blue and red lines show the data before and after exposure to an atmospheric environment of ~50% relative humidity for 5 days, respectively. (c) Absorption and photoluminescence spectra of a (C₆H₅CH₂NH₃)₂PbI₄ perovskite film spin-coated on a glass substrate. (d) Femtosecond PL decay trace of a (C₆H₅CH₂NH₃)₂PbI₄ perovskite film spin-coated on a glass substrate. Reproduced with permission from reference 40.

M. 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 non-radiative recombination. The quasi-2D perovskite material studied was synthesized using phenylethylammonium (C₆H₅C₂H₄NH₃) as a spacer. The device’s EL and the photoluminescence quantum yield (PL-QY) were tuned by varying n values and the number of PbI₄ layers in the quasi-2D perovskite. It was found that significantly higher values of PL-QY, e.g., 10.1% and 10.6 % were achieved in the case of quasi-2D-layered materials with n=3, and n=5, respectively, as compared with less than 0.1% for n=1 under the same excitation intensities of 6 mW/cm². The devices fabricated with an ITO/thin TiO₂/ (PEA₂(MA)ₙ₋₁PbnI₃n+1)/poly (9,9’-octylfluorene) F8/MoO₃/Au structure performed well, achieving 8.8% EQE and 80 W sr⁻¹m⁻² radiance, in the near infrared (NIR) region.
D. Liang et al.\textsuperscript{44} utilized quantum-confined 2D perovskite, based on 2-phenylethlammonium lead bromide (PEA.PbBr\textsubscript{4}), to realize color-pure violet LEDs. The material was found to assemble in well-confined quantum-well structures with an energy diagram, as shown in Figure 5a and b, respectively, with a repeating dielectric spacer layer, sandwiching 3D PbBr\textsubscript{6} octahedra in between. The better-performing high-quality perovskite layer with a millimeter grain size has been achieved through a solvent annealing procedure, in the presence of DMF vapors.

![Figure 5: (A) Crystal structure of 2-phenylethlammonium lead bromide, (PEA)\textsubscript{2}PbBr\textsubscript{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 the 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)\textsubscript{2}PbBr\textsubscript{4}. Reproduced with permission from reference 44.](image)

The 2D materials exhibited an entirely different morphology and topographical behavior when utilizing a direct baking and solvent annealing method, using AFM and SEM. The films...
deposited through the direct baking of perovskite were found to be smoother than those deposited using solvent annealing in the presence of DMF, which in turn, was found to drastically 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 404 nm, and an intense PL band at 407 nm, which were attributed to the high PL-QY of the films, from 10% for thin film and 26% for the nanoplates. The PL lifetimes of both films have been studied with the help of wavelength-resolved time-correlated single photon counting, and were found to be about 2 times longer (1.27 ns vs. 0.62 ns) in the nanoplates.

The cross-section SEM of the fabricated LED devices and the energy level diagram of different layers are shown in Figure 6a and b, respectively. Both the PL and EL spectra of the devices are shown in Figure 6c, indicating a blue shift of 3 nm in the PL maxima as compared with the EL maxima; which was attributed to the 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 devices with nano-plates is about 20 times higher than that fabricated through thin films, i.e., 0.04 % vs. 0.002 %. The low EQE for the pure violet LED is comparable to similar LEDs formed with other materials, such as Cds/ZnS core shell quantum dots.45
Figure 6: (A) Cross-sectional SEM image of the (PEA)$_2$PbBr$_4$ LED devices. The scale bar is 200 nm. (B) Energy-level diagram for the (PEA)$_2$PbBr$_4$ LED devices. The valence band edge of (PEA)$_2$PbBr$_4$ 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)$_2$PbBr$_4$ nanoparticles obtained from DMF vapor annealing operating at 6 V. The EL and PL peaks are located at 410 and 407 nm, respectively. The weak EL peak at 375 nm is from TPBi, consistent with its PL (gray curve). The inset shows a picture of uniform violet light emission from a (PEA)$_2$PbBr$_4$ LED device. (D) Current–voltage (J–V) dependence (red symbols) and EQEs (blue symbols) for LEDs fabricated with a (PEA)$_2$PbBr$_4$ thin film (open symbols) and nanoplates (solid symbols). Reproduced with permission from reference 44.

H. Hu et al.\textsuperscript{46} recently reported on tunable LEDs with fine emission and different color regions, using the 2D perovskite structure (the $n$ values were in the range of $n=1$ to $n=6$) achieved through butylammonium iodide (C$_4$H$_9$NH$_3$I) as a spacer. The high-quality films deposited through the fast deposition process were characterized using XRD, AFM, absorption, and PL. The authors correlated the presence of an intense absorption peak at about 510 nm with a strong photon-exciton interaction confined within the 2D quantum wells, resulting in a long lifetime and a large exciton binding energy of 300 meV.\textsuperscript{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.\textsuperscript{48} demonstrated a stable red LED in contrast to previous reports, which reported some difficulties in achieving a stable red LED due to the phase separation of the Iodide/Bromide counterparts. A maximum 214 cd/m$^2$ luminance has been 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 the 2D perovskite.

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

**Table 1:** LED architectures and performance parameters of different low-dimensional perovskite types.

<table>
<thead>
<tr>
<th>Color</th>
<th>Device Architecture including the perovskite type</th>
<th>$\lambda_{\text{max}}$ of EL (nm)</th>
<th>$V_{\text{on}}$ (V)</th>
<th>Max. EQE (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green</td>
<td>ITO/PEDOT:PSS/(C$_6$H$_5$CH$_2$NH$_3$)$_2$PbI$_4$/Bphen/Al</td>
<td>526</td>
<td>2.8</td>
<td>0.005</td>
<td>37</td>
</tr>
<tr>
<td>Red</td>
<td>ITO/TiO$_2$/(PEA)$<em>3$(MA)$</em>{n-1}$Pb$<em>n$I$</em>{3n+1}$/F8/MoO$_3$/Au</td>
<td>735 ($n=3$) 755 ($n=5$) 760 ($n=10$) 770 ($n=40$)</td>
<td>3.8</td>
<td>8.8</td>
<td>40</td>
</tr>
<tr>
<td>Color</td>
<td>ITO/PEDOT:PSS/(PEA)$_2$PbBr$_4$/TPBi/Ca/Al</td>
<td>410</td>
<td>2.5</td>
<td>0.04</td>
<td>41</td>
</tr>
<tr>
<td>---------</td>
<td>------------------------------------------</td>
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</tr>
<tr>
<td>Red</td>
<td>ITO/PEDOT:PSS/poly-TPD/(BA)$_2$(MA)$_2$Pb$<em>3$I$</em>{10}$/TPBi/LiF/Al</td>
<td>700</td>
<td>2.7</td>
<td>2.29</td>
<td>43</td>
</tr>
<tr>
<td>Green</td>
<td>ITO/PEDOT:PSS/poly-TPD/(BA)$_2$(MA)$_2$Pb$<em>3$Br$</em>{16}$/TPBi/LiF/Al</td>
<td>523</td>
<td>3.3</td>
<td>1.01</td>
<td>43</td>
</tr>
<tr>
<td>Blue</td>
<td>ITO/PEDOT:PSS/poly-TPD/(BA)$_2$(MA)$_2$Pb$_3$Br$_7$Cl$_7$/TPBi/LiF/Al</td>
<td>468</td>
<td>5.2</td>
<td>0.01</td>
<td>43</td>
</tr>
<tr>
<td>Red</td>
<td>ITO/Poly TPD/BAI:MAPbI$_3$/TPBi/LiF/Al</td>
<td>748</td>
<td>5-6.5</td>
<td>10.4</td>
<td>50</td>
</tr>
<tr>
<td>Green</td>
<td>ITO/Poly TPD/BABr:MAPbBr$_3$/TPBi/LiF/Al</td>
<td>513</td>
<td>5-6.5</td>
<td>9.3</td>
<td>50</td>
</tr>
<tr>
<td>Red</td>
<td>ITO/ZnO:PEIE/NFPI$_7$/TFB/MoOx/Au</td>
<td>786</td>
<td>2.3</td>
<td>9.6</td>
<td>51</td>
</tr>
<tr>
<td>Red</td>
<td>ITO/ZnO:PEIE/NFPI$_6$B/TFB/MoOx/Au</td>
<td>763</td>
<td>2.6</td>
<td>11.7</td>
<td>51</td>
</tr>
<tr>
<td>Green</td>
<td>ITO/PEDOT:PSS/PEA$<em>2$(MA)$</em>{n-1}$Pb$<em>n$Br$</em>{3n+1}$/TPBi/LiF/Al</td>
<td>520 &amp; 526 For $n=3$ &amp; $5$ respectively</td>
<td>-</td>
<td>7.4</td>
<td>52</td>
</tr>
</tbody>
</table>

### 4.2 Low-dimensional halide perovskite in photodetectors

Another possible application using 2D perovskite is with photodetectors. P. Li et al.\textsuperscript{49} reported on high-performance photodetectors based on 2D nanosheets of MAPbI$_3$. The extremely thin nanosheets, having about a 20 nm thickness, were achieved through the chemical vapor deposition (CVD) method on already deposited PbI$_2$ crystals on top of SiO$_2$ sheets, - to achieve planar devices, whereas when using ITO as the substrate, it was possible to fabricate vertical devices. The substrate preparation step involved the sequential processes of photoetching the ITO followed by O$_2$ plasma etching and removal of photoresist; then the perovskite layer has been deposited on these substrates using two step method followed by counter electrode evaporation, in order to complete the photodetector device.

The photo response was higher for vertical devices than for planar devices. The highest responsivity of 36 mA/W was achieved at an excitation power rate of 50.82 $\mu$W, due to the low trap density and short carrier diffusion length in 2D perovskites.
5. Summary and outlook

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

The 2D perovskite has been well known for many years. However, due to the remarkable power conversion efficiency of the 3D perovskite, the 2D perovskite has been studied less, owing to the breakthrough of its counterparts. This paper discusses 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 using these materials.

The possibility of synthesizing 2D perovskite using various organic barriers opens up a whole new batch of interesting materials with huge potential for optoelectronic applications. This potential is even more pronounced than their 3D perovskite counterparts, since 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, the 2D perovskite, as discussed previously in this mini review, can use organic barriers with different chain lengths, aromatic rings, and double bonds, among other structures, which results in different optical, structural, and electronic properties.

Moreover, recently the 2D perovskite exhibited efficiencies similar to the 3D perovskite in solar cells, where the big advantages are related to their better stability in comparison with the 3D perovskite. The 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 PV field. Taking advantage of their properties, the 2D perovskites are also promising candidates for LED devices, mainly due to their high radiative recombination as a result of the confined 2D quantum well.

These 2D and quasi-2D 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, the 2D perovskite requires only simple and easy processing methods, which was one of the major reasons for the attractiveness of 3D perovskite. This enables them to be excellent candidates for stable perovskite that can be used for high-efficiency solar cells and optoelectronic applications.
References


