Low-dimensional metal halide perovskites and related optoelectronic applications

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Abstract
Low-dimensional materials have pivotal significance in modern photonic, electronic, and optoelectronic areas due to their unique properties of the scale effect. Metal halide perovskites have revived in the optoelectronic fields recently, drawing intensive attention in photovoltaic devices, light-emitting diodes, lasers, photodetectors, and so on. Compared to their three-dimensional counterparts, the role of low-dimensional perovskites is becoming crucial, requiring a comprehensive understanding and exploration unceasingly. In this review, we examine low-dimensional perovskite of different forms and clarify various synthesis methods with morphological and dimensional control. Additionally, we also summarize potential optoelectronic applications based on their advantageous optical/electrical properties and enhanced mechanical integrity and stability. Finally, we propose a future perspective and possible developing directions in the exploration of novel perovskite-derived materials, new physics, and promising applications.

KEYWORDS
applications, low-dimension, metal halide perovskites, synthesis

1 | INTRODUCTION

Perovskite, which refers to specific compounds that possess a formula of ABX₃ (A and B sites are cations, and X site is anion) and the identical structure as CaTiO₃, has been investigated for more than a century. In recent years, organic-inorganic metal halide perovskites, as one of the various types, have attracted much attention due to their unique properties and remarkable device performances. In 2009, Kojima et al. utilized lead halide perovskite as sensitizers in dye-sensitized solar cells, achieving a solar-to-electricity power conversion efficiency (PCE) of 3.8%. This research marks the new renaissance of metal halide perovskites first in PV devices. From that time on, the development of perovskite solar cells has dramatically ascended, achieving a certified PCE up to 25.2% (Best Research-Cell Efficiencies (NREL, 2019) https://www.nrel.gov/pv/assets/pdfs/best-research-cell-efficiencies.20190802.pdf). Due to the unique optoelectronic merits like high absorption coefficient, good defect-tolerant properties, ease of fabrication, and so on, metal halide perovskites have extensive applications not only in PV field but also in other optoelectronic devices such as light-emitting diodes (LEDs), photodetectors, nanolasers, and so on.

Bulk three-dimensional (3D) metal halide perovskites have a general structural formula of ABX₃, where A site...
is a cation, typically the organic methylammonium (MA$^+$), formamidinium (FA$^+$) or inorganic cesium (Cs$^+$). B site is metal, typically lead (Pb$^{2+}$), or tin cations (Sn$^{2+}$), and X site is the halide like chloride (Cl), bromide (Br), and iodide (I). The term “3D” here focuses on the materials themselves and emphasizes the connected ways where [BX$_6$]$^{4-}$ octahedra consisting of one B cation, and six X anions are combined through corner sharing to form a 3D network. The A cation occupies the site in the middle of eight octahedra, and each element here needs to owe the proper valence state to keep a whole charge balance.

To predict the 3D structure forming possibility, Goldschmidt tolerance factor ($t$) and octahedral factor ($\mu$) are used as empirical rules. The definitions of $t$ and $\mu$ are as following: 

$$t = \frac{R_A + R_X}{\sqrt{2(R_B + R_X)}}, \quad \mu = \frac{R_B}{R_X}$$

where $R_A$, $R_B$, and $R_X$ are the effective radii of the A, B, and X ions, respectively. For a well-established 3D network, $t$ and $\mu$ are usually in the range of 0.8-1.0 and 0.44-0.9, respectively.

Non-perovskite structures are often observed for improper-sized ions, for example, large A cations like CH$_3$CH$_2$NH$_3^+$ ($t > 1.0$) and small A cations like Rubidium ($t < 0.8$) will both lead to the collapse of the 3D structured network. As observed empirically, distinguished advantages suitable for optoelectronics often vanish when switching to the non-perovskite structures.

“Low-dimensional” perovskites refer to the perovskite compounds with at least one reduced dimension, in contrast to that with three unlimited extensions. The term “low-dimensional” often leads to confusion due to its diverse meanings in different situations. In this review, we classify low-dimensional perovskites from two aspects: “material-level” and “structure-level” low dimensionalities.

The “material-level” low dimensionality emphasizes the perovskite material itself, underlining the building blocks of the perovskites that the individual components should have at least one dimension down to the molecular level. Specifically, these consisting parts made of [BX$_6$]$^{4-}$ octahedra usually exist in several forms, such as two-dimensional (layers), one-dimensional (wires), or separately zero-dimensional (polyhedrons) styles (Figure 1A).

Differently, “structure-level” low-dimensional perovskites emphasize the final morphologies and commonly refer to those nanostructures of nanoplatelets/nanosheets, nanowires/nanorods, and nanocrystals (Figure 1B). Mostly, these “structure-level” low-dimensional perovskites are made up of the 3D networks of corner-sharing.

**FIGURE 1** A, Schematic illustration of “material-level” low-dimensional perovskites and 3D perovskite. B, Schematic illustration of “structure-level” low-dimensional perovskites and perovskite bulk materials
[\text{BX}_6]^{2-} \text{ octahedra}, the same as that in bulk ABX$_3$ perovskites. In some specific cases, these nanostructures also consist of “material-level” low-dimensional individual species (layers, wires, or polyhedrons) as well.\textsuperscript{54} From the above discussion, “structure-level” and “material-level” low dimensionalities are used to elaborate on different aspects and are not on opposite sides due to the partial overlap. In the following section, when referring to “structure-level” low-dimensional perovskites, we also use expressions such as nanoplatelets, nanowires, andnanocrystals to distinguish from “material-level” low-dimensional perovskites.

Compared to 3D counterparts commonly used, low-dimensional perovskites possess additional properties, mainly originating from their shape diversity and quantum confinement effects.\textsuperscript{55-58} For example, due to the widely adjustable dimensions and sizes, low-dimensional materials usually own feasibly tunable bandgaps, enriching the wavelength range of absorption and emission.\textsuperscript{59-61} Owing to the enlarged Coulombic force between electrons and holes, these electron-hole pairs have much higher binding energy and consequent high photoluminescent efficiency, which are desired for luminescent applications.\textsuperscript{62-65} Also, strong anisotropic nature, together with enhanced surface-volume-ratio, could provide better contacts and smooth charge transport channel.\textsuperscript{66,67} Finally, better crystallinity with reduced trap density and enlarged mechanical stability are often observed in low-dimensional material, greatly improving the optoelectronic device longevity and beneficial for flexible electronics.\textsuperscript{68-71}

In this review, we will focus on the “structure-level” low-dimensional perovskites regardless of the consisting individuals (bulk, layers, wires, or polyhedrons). Meanwhile, some perovskite bulk forms consisting of “material-level” low-dimensional components are also selectively discussed in the following section.

2  \textbf{2D METAL HALIDE PEROVSKITES}

As the thickness reduces to several unit cells, the quantum confinement effect typically leads to larger binding energy, higher photoluminescence (PL), and increased bandgaps.\textsuperscript{71} Perovskite nanosheets or nanoplatelets can be thought by minimizing the thickness of bulk 3D ABX$_3$ perovskite to a large extent. When they are extremely thin, the formula is no longer the ABX$_3$ but with a finite value of $n$: $A_{n-1}B_nX_{3n+1}$.\textsuperscript{46} These thin nanosheets typically consist of similar networks as 3D counterparts, with two A cations terminated on the top and bottom sides.

In addition to these nanosheets, there is another “material-level” low type of two-dimensional (2D) perovskite, Ruddlesden-Popper (RP) phase perovskites, which have a chemical formula of $L_2A_{n-1}B_nX_{3n+1}$ (L is the long-chain cation and A is the smaller cation that can be fitted into the 3D lattice, like MA$^+$ or FA$^+$). The L normally has ammonium cations that can react with the terminated $[\text{BX}_6]^{2-}$ corner-shared layer and fit the periphery of these octahedra. These RP-type perovskites can be assembled into a bulk crystal or other nanostructures through the van der Waals interaction of each layer, keeping quantum confinement effects unchanged.\textsuperscript{44,54,72-74} In this section, we concentrate on the synthesis methods and corresponding applications of nanoplatelets based on 3D networks and partially discuss the 2D RP-phase assembled bulk perovskites when referring to some optoelectronic applications.

2.1  \textbf{Synthesis methods}

2.1.1  \textbf{All vapor-phase synthesis method}

The bottom-up process is found to be feasible to achieve the desired 2D nanostructures. Considering the van der Waals layered nature of lead halides, it appears an effective way to acquire perovskite nanosheets with a start from PbX$_2$ nanoflakes (X = Cl/Br/I).\textsuperscript{75-77} In 2014, Ha et al. developed a two-step method, combining chemical vapor deposition (CVD) and gas-solid reaction, to grow perovskite nanoplatelets (Figure 2A).\textsuperscript{75} The authors first grew PbI$_2$ nanoplatelets on the muscovite mica substrates by van der Waals epitaxy in a vapor transport chemical deposition system. Then, they converted the as-formed PbI$_2$ nanoplatelets into perovskites by a gas-solid reaction with methylammonium iodide (MAI) molecular gas, slightly increasing the thickness after the incorporation of MAI molecular (Figure 2B).\textsuperscript{75} The prepared perovskite nanoplatelets exhibit a lateral dimension of 5-30 $\mu$m and a thickness from dozens of to several hundreds of nanometers. By replacing the muscovite mica by SiO$_2$/Si substrates and altering the synthesis temperature and time, Niu et al. could precisely tune the thickness of perovskite nanoplatelets from few layers to several nanometers.\textsuperscript{76} Besides, when employing rough-surfaced substrates, free-standing and large-scale PbI$_2$ nanosheets were synthesized by Lan et al. through the manipulation of microenvironment (Figure 2C).\textsuperscript{77} Complete conversion to free-standing perovskite nanoflakes by CVD provides the promising potential for photon-detected applications.
2.1.2 Combined solution- and vapor-phase synthesis method

Thin PbI$_2$ nanoplatelets with the thickness down to monolayer can also be obtained by a facile solution process (Figure 2D). Saturated PbI$_2$ aqueous solution was cast on a substrate, and 2D PbI$_2$ nanosheets would nucleate at an elevated temperature. Similar to the vapor-conversion process above, 2D MAPbI$_3$ perovskite nanosheets were formed by intercalating the MAI molecules into PbI$_2$ nanosheets under a gas atmosphere. Later, an impressive work by Wang et al. demonstrated well-patterned perovskite microplatelet arrays on a periodic substrate (Figure 2E). Specifically, the substrates were partially treated with periodic hydrophilic patterns, where the PbI$_2$ seeds emerged after the seeding solution flew over.
Afterward, a common vapor reaction process by MAI gas converted PbI2 microplates into the desired perovskite plates. The successful realization of the periodic perovskite patterns proves the potential applications in integrated electronics.

### 2.1.3 Exfoliation method

Different from the inherent ionic bond of nanoplatelets, the weak van der Waals interaction between neighboring layers makes it possible for RP type perovskite to be exfoliated into ultrathin nanosheets. Niu et al. produced one to a few layers of thin flakes from \((\text{C}_6\text{H}_9\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbI}_4\) crystals (Figure 3A-C). Hexagonal RP type \((\text{C}_6\text{H}_9\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbI}_4\) perovskite microcrystals with 30 μm lateral size were first synthesized, followed by a micromechanical exfoliation technique to create ultrathin flakes. This method is rather suitable for the investigation of fundamental properties but inconvenient for high production due to the uncontrollable size and thickness.

### 2.1.4 Direct solution growth method

In 2015, Dou et al. proposed a direct solution growth method to synthesize atomically thin RP type \(\text{BA}_2\text{PbI}_4\) (\(\text{BA} = \text{C}_4\text{H}_9\text{NH}_3^+\)) perovskite nanosheets. A much diluted precursor in ternary organic solvents was cast on flat substrates, where acetonitrile (ACN) and chlorobenzene were used to reduce the solubility of \(\text{BA}_2\text{PbI}_4\) in dimethylformamide (DMF) and promote the crystallization (Figure 3D). Thus, a single-unit layer, with a thickness of ~1.6 nm, was successfully demonstrated. Based on this work, Chen et al. further studied the critical factors systematically, including crystallization temperature, solvent ratio, and polarity on the growth dynamics (Figure 3E). They assumed that the formation of large-size thin sheets was governed by the effects of diffusion-mechanism-dominated branched growth, together with CAN-induced c-axis suppression. Under the optimized condition, 2D \(\text{BA}_2\text{PbBr}_4\) perovskites with the lateral sizes up to 40 μm and thicknesses down to a few nanometers were obtained. These works above suggest that the solution growth method can be suitable to achieve high-quality perovskite nanosheets with controllable thickness.

### 2.1.5 Colloidal growth method

Due to the great success in the synthesis of inorganic quantum dots like CdSe and ZnSe, the colloidal growth method has vital importance in the perovskite nanostructure fabrication. In 2015, Tyagi et al. adapted a precipitation method used for perovskite nanoplatelet
synthesis, where octylammonium bromide (OABr) was chosen as the long-chain ligands. Later, Sichert et al. synthesized MAPbBr$_3$ nanoplatelets by a modified process where they added a mixed solution of PbBr$_2$, OABr, and MABr in DMF into toluene dropwise (Figure 4A). The thicknesses of these nanoplatelets were well controlled from one to several units by varying the adding amount of OABr. Bekenstein et al. reported the colloidal synthesis of highly luminescent (photoluminescent quantum yield [PLQY] 84%) inorganic CsPbX$_3$ nanoplatelets with the thickness of 1-5 unit cells, showing adjustable PL emissions due to strong quantum size effect (Figure 4B). A facile anion exchange process further promoted the PL emissions covering the entire visible spectrum. The systematic investigations facilitated the following development of the CsPbX$_3$ nanoplatelet synthesis, with a more precise thickness control (Figure 4C) and an enlarged lateral size up to micrometer range (Figure 4D-E).

2.2 Applications of 2D metal halide perovskites

Solar cells employing 3D perovskites have achieved considerable improvements in the past few years, yielding a certified PCE up to 25.2%. Along with the rapid PCE development, the instability problem has been proposed
as a considerable issue. Compared to the traditional 3D ABX₃ perovskite, 2D RP layered perovskite has a much more enhanced moisture tolerance and can improve the stability to a certain extent. In addition to this benefit, the confinement in 2D perovskite will bring up large binding energy and improve the photoluminescent efficiency, which is promising for the application of emissions like LEDs and lasers.

In the following section, we will discuss the optoelectronic applications based on 2D perovskites, including not only nanosheets or nanoplatelets but also some unique forms of RP type perovskites.
<table>
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<th>Structures</th>
<th>Device configuration</th>
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<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
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2.2.1 Solar cells

The first generation of solar cells utilizing an RP type perovskite PEA2MA2Pb3I10 (PEA = C6H5(CH2)2NH3+) as the absorber was fabricated by Smith et al. (Figure 5A) exhibiting a PCE of 4.73%.93 Although this efficiency falls behind that based on 3D perovskites, the moisture tolerance, which is essential for large-scale manufacture and broad commercialization, shows much superior performance than its bulk counterpart.93 Later, Cao et al. reported another RP type perovskite-based solar cell by using a relatively shorter organic cations BA (Figure 5B). Due to the self-assembly nature, 2D compounds with n > 2 values (BA2MAn-1PbnI3n+1) were formed with preferential growth orientation, beneficial for charge transport and formation of smooth thin films.94 Interestingly, when adopting a planar structure, the photovoltaic (PV) parameters were much poorer compared to the mesoporous structure, attributed to the short diffusion length of photocarriers in the 2D RP type perovskite.94 Tsai et al. proposed a similar hypothesis that insufficient charge transport could lead to worse performance arose from the nonideal layer orientation, where organic cations acted like insulating spacing layers between the conducting inorganic slabs. By applying a proposed hot-casting method here (Figure 5C), they produced BA2MAn-1PbnI3n+1 thin films of near-single-crystalline quality, where the crystallographic planes of the inorganic perovskite had a preferential orientation perpendicular to both contacts.98 In a planar structure employing BA2MA3Pb4I13 as absorber, they obtained a PCE of 12.52%, among the highest efficiency of low-dimensional perovskite solar cells at that time (Figure 5D). Unencapsulated and encapsulated devices both exhibited much-enhanced stability when exposed to humidity and constant illumination. As the layer number n can effectively affect the device performance and stability, a systematical exploration to understand this

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<td>FAPbI(_3)</td>
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<tr>
<td>CsPbI(_3)</td>
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<td>CsPbI(_3)</td>
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<td>CsPbI(_3)</td>
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<td>CsPbI(_3)</td>
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<tr>
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</tr>
<tr>
<td>CsPbI(_3): FAPbI(_3)</td>
</tr>
</tbody>
</table>

Note: \(J_{sc}\), short-circuit current; \(V_{oc}\), open-circuit voltage; FF, fill factor; PCE, power conversion efficiency.
correlation and inherent mechanism is in a request. Quan et al. fabricated quasi-2D perovskite films that exhibited enhanced stability without sacrificing the high performance of 3D MAPbI3 perovskites (Figure 5F).99 Confirmed by density functional theory, the instability issue of 3D perovskites originates from the low formation energy and becomes aggravated when taking high humidity into account (Figure 5E). The addition of larger organic cation to form quasi-2D perovskite could enlarge the formation energy owing to the appreciable van der Waals forces that conferred enhanced stability. This work provides one possible elucidation of why 2D or quasi-2D perovskites own improved stability, especially when exposed to high moisture. For clear comparison, we summarize the key parameters of solar cells based on 2D perovskites in Table 1.

### 2.2.2 | Light-emitting diodes

Enlarged binding energy and strong PLQY from quantum confinement make 2D perovskites suitable for the applications of LEDs.131-133 The first 2D RP perovskite-based LEDs can date back to the mid-1990s, where Era et al. demonstrated the device by incorporating a layered perovskite compound PEA2PbI4, showing an emission peak at 520 at liquid-nitrogen temperature.131 However, when driven at room temperature, the electroluminescence (EL) efficiency became rather low, which could be explained by the thermal quenching of photoluminescent in the perovskite film. Thus, fabricating efficient LEDs with certain EL efficiency at room temperature is a demanding trend. Liang et al. improved the crystal quality by converting polycrystalline PEA2PbBr4 thin films into single-crystalline micro-sized nanoplates via solvent vapor annealing and showed efficient room-temperature violet EL at 410 nm (Figure 6A).132 Compared to the pure phase RP perovskite components (one value of n only), polycrystalline RP perovskite films containing multiple phases (multiple values of n) have superior light-emission performance.134-137,139-141 Yuan et al. and Huang et al. independently reported LEDs incorporated with mixed layered perovskite materials, displaying impressive performance and stability. The mixed compounds act like a photocarrier concentrator, funneling the charge carriers from high-bandgap materials to the lowest-bandgap ones and boosting the external quantum efficiency (EQE) to 8.8% and 11.7% (Figure 6B-C), respectively.134,135 Jiang et al. tuned the “A-site” cation by using a Rubidium-Cesium alloyed perovskite, demonstrating a spectra-stable blue LED with a peak EQE of 1.35% (Figure 6D).136 In addition to the composition engineering, other strategies like surface passivation, crystallite tailoring, structure engineering, and so forth were also applied for performance and longevity improvement.137-141 Yang et al. utilized trioctylphosphine oxide treatment to passivate the surface of quasi-2D PEA2 (FAPbBr3)n-1PbBr4 films, achieving an EQE of 14.36%.140 Xiao et al. added large-group ammonium as a surfactant to constrain the growth of 3D grains, producing smooth films consisting of crystallites with a size of about 10 nm.141 Through the incorporation of small ions such as sodium (Na+) to substitute the large organic molecules, Wu et al. overcame the charge transport issue resulting from the insulating long-chain cation and achieved a high EQE of 15.9% (Figure 6E,F).137 To further boost the EL efficiency of LEDs, Zhao et al. demonstrated a perovskite-polymer bulk heterostructure (PPBH) to suppress non-radiative recombination channels and obtained an EQE up to 20.1% (Figure 6G).138 Bipolar host materials like PVK: PBD were also incorporated for the protection, enabling glove-box free fabrication of LEDs, with efficient green photoluminescence and long-term stability.142 Detailed key parameters of 2D perovskite-based LEDs are summarized in Table 2.

### 2.2.3 | Photodetectors

Owing to the large absorption coefficient, high carrier mobility, and good compatibility with flexible substrates, perovskite nanosheets are also appropriate for photodetectors.77,159-161 In 2015, Liu et al. demonstrated a thin MAPbI3 nanosheet-based photodetector through a combined solution process and vapor-phase conversion method (Figure 7A).78 Under the incidence at 405 and 532 nm, the current density was significantly increased, showing photo responsivities of 22 and 12 AW−1 (at 1 V) and fast response time (Figure 7B,C). Wang et al. grew 2D perovskite microcrystals on patterned electrodes (Figure 7D), creating independently addressable photodetector arrays and functional field-effect transistors (Figure 7E,F).78 In addition, photodetector based on inorganic perovskite nanosheets (like CsPbX3, X = I/Br/Cl) has analogous performances compared to their organic counterparts.161-163 Due to the ultra-smooth surface and high optical response, a flexible detector based on monolayer and few-layer CsPbBr3 nanosheets showed superior electrical stability even after 10 000 times of bending (Figure 7G,H).161 The following optimization to increase carrier extraction and transport by a combination of CNTs and CsPbBr3 nanosheets (Figure 7I) enabled a flexible photodetector with an EQE and responsivity as high as 7488% and 31.1 AW−1 (Figure 7J).162 A summary of the key parameters of photodetectors based on 2D perovskites is exhibited in Table 3.
Lasers

It is well known that well-faceted nanowires with suitable diameters support predominantly axial Fabry-Pérot waveguide modes in nanolasers. Apart from this, whispering-gallery mode existing in micro/nanodisks can utilize successive total internal reflection along the circumference and provide high cavity quality factor. In 2014, Zhang et al. realized room-temperature near-infrared nanoplatelet lasers using MAPbI₃-aXₐ (X = I, Br, Cl) nanoplatelets (Figure 8A). This wavelength-tunable nanolaser (Figure 8B) could be easily integrated onto conductive platforms like Si, Au, and indium tin oxide, promising for the integrity of existing Si technology. Later, the same group fabricated all inorganic nanoplatelet lasers, where the whispering-gallery mode cavities showed multicolor lasing (Figure 8C) with a low threshold (~2 μJ cm⁻²) and high spectra coherence (~0.14-0.15 nm). 2D RP type perovskites widely integrated in LEDs are also desirable for the application of lasers for its high PL efficiency. Zhang et al. demonstrated a novel microring laser array based on the (BA)$_2$(MA)$_n$PbnBr$_{3n+1}$ perovskites (Figure 8D). For a given value of n, the practically mixed composition render photocarriers to transfer from the high-bandgap perovskites to the lowest-bandgap ones, enabling the

<table>
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<tr>
<th>Materials</th>
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<th>EL $\lambda_{\text{max}}$ (nm)</th>
<th>Max EQE (%)</th>
<th>Max CE (cd A⁻¹)</th>
<th>Max PE (lm W⁻¹)</th>
<th>Max L (cd m⁻²)</th>
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Note: EL, electroluminescence; CE, current efficiency; PE, power efficiency; L, luminance; EQE, external quantum efficiency.

2.2.4 | Lasers

It is well known that well-faceted nanowires with suitable diameters support predominantly axial Fabry-Pérot waveguide modes in nanolasers. Apart from this, whispering-gallery mode existing in micro/nanodisks can utilize successive total internal reflection along the circumference and provide high cavity quality factor. In 2014, Zhang et al. realized room-temperature near-infrared nanoplatelet lasers using MAPbI₃-aXₐ (X = I, Br, Cl) nanoplatelets (Figure 8A). This wavelength-tunable nanolaser (Figure 8B) could be easily integrated onto conductive platforms like Si, Au, and indium tin oxide, promising for the integrity of existing Si technology. Later, the same group fabricated all inorganic nanoplatelet lasers, where the whispering-gallery mode cavities showed multicolor lasing (Figure 8C) with a low threshold (~2 μJ cm⁻²) and high spectra coherence (~0.14-0.15 nm). 2D RP type perovskites widely integrated in LEDs are also desirable for the application of lasers for its high PL efficiency. Zhang et al. demonstrated a novel microring laser array based on the (BA)$_2$(MA)$_n$Pb₅Br₃n+1 perovskites (Figure 8D). For a given value of n, the practically mixed composition render photocarriers to transfer from the high-bandgap perovskites to the lowest-bandgap ones, enabling the
population inversion for stimulated emission. Thanks to the well-defined geometries and inherent carrier concentration effect, the microring laser behaved well as an efficient whispering-gallery-mode laser with a very high quality factor (~2600) and low lasing threshold (~13.6 μJ cm⁻²) simultaneously.

As another basic building block, perovskites nano-wires or nanorods have been widely investigated for their tunable bandgaps, anisotropic electrical/optical properties, and outstanding photoluminescent efficiency. In this section, we will go through the progress on the 1D perovskites, including nanowires and nanorods.

### 3.1 Synthesis methods

#### 3.1.1 Solution-phase synthesis method

The first synthesis of metal halide perovskite nanowires (MAPbI$_3$) was demonstrated by the Horváth group in 2014 (Figure 9A-E). Two sets of MAPbI$_3$ nanowires with mean diameters of 50 and 400 nm and lengths up to 10 μm were fabricated by a solution-mediated crystallization process (Figure 9F-I). A thin saturated solution film...
of MAPbI$_3$ in DMF was confined by two glass slides, and the nanowires came into crystallization while gradually sliding the upper glass to expose the liquid to air. It was assumed that the nanowire growth was due to the directional effect of DMF that an internal complex with the methyamine group was formed during the crystallization process. A great breakthrough in halide perovskite nanowire synthesis was put forward by

**FIGURE 8** A, Schematic of the MAPbX$_3$ perovskite nanoplatelet-based laser. The whispering-gallery-mode is illustrated in these nanoplatelets. B, Optical images of two CH$_3$NH$_3$PbI$_3$ nanoplatelets under the illumination of white light (upper) and incidence laser (bottom). Clear diffraction patterns can be seen inside the whispering-gallery-mode cavity. Reproduced with permission. Copyright 2014 American Chemical Society. C, Lasing spectra from CsPbX$_3$ nanoplatelets with different compositions. The insets are photographs of the corresponding lasers. Reproduced with permission. Copyright 2016 Wiley-VCH. D, Photoluminescence (PL) images of 3 × 3 microring laser arrays. Spatial interference patterns from all the microrings indicate the coherent outputs. The right figure shows the PL spectra of the ring labeled as 8 vs pump intensity. Reproduced with permission. Copyright 2018 Wiley-VCH.
Fu et al. (Figure 9J) They proposed a dissolution-recrystallization model to grow single-crystalline MAPbI$_3$ nanowires. The pre-deposited poly-crystalline lead iodide (PbI$_2$) film was immersed into MAI/isopropanol solution with different concentrations, where high concentration will lead to the formation of thermodynamically
favorable PbI$_2^-$ complex ions after reacting with superfi-
cial MAPbI$_3$ and PbI$_2$. As PbI$_2^-$ ions became over-
saturated, they would react with MA$^+$ and facilitate the
anisotropic growth of nanostructures (Figure 9K).$^{185}$
Starting from this method, different kinds of perovskite
nanowires were successfully synthesized. For example,
stabilized FAPbI$_3$ nanowires (Figure 9L) and robust
inorganic CsPbX$_3$ nanowires (Figure 9M) were both suc-
cessfully demonstrated by modifying the precursor com-
positions and concentrations feasibly.$^{186,187,190-194}$

### 3.1.2 Vapor-phase synthesis method

In the past years, the vapor-phase synthesis method
was widely used to fabricate high-quality all inorganic
nanowires like silicon, tin oxide, and zinc oxide and
was then modified for the perovskite nanowire synthe-
sis.$^{195-198}$ In 2014, Ha et al. successfully demonstrated
MAPbX$_3$ perovskite nanowires through a two-step
vapor phase method, where lead halide (PbX$_2$) nano-
wires were first deposited by CVD (Figure 10A-B) and
then converted into perovskite through the gas-solid
reaction with amine halide molecules.$^{75}$ Compared to
this with two processes, direct vapor-phase growth is
also effective for nanowire fabrication. It is commonly
used for traditional inorganic nanowire synthesis and
unsuitable for organic halide perovskite with low
decomposition temperature. However, when applied to
all inorganic thermal-stable halide perovskite, this
approach will become more feasible.$^{172,173,201}$ Chen et
al. reported a vapor-phase epitaxial growth of horizon-
tal single-crystalline CsPbX$_3$ nanowires and microwires
with controlled crystallographic orientations.$^{173}$ The
asymmetric lattice mismatch between CsPbX$_3$ and mica
substrates leads to strict growth along the [110] direc-
tion and unlimited growth along the [001] direction,
forming different morphologies such as single nano-
wires, Y-shaped branches, interconnected nanowire,
or microwire networks (Figure 10C). Later, based on
a similar direct vapor-phase synthesis, Shoaib
et al. fabricated ultralong CsPbBr$_3$ nanowires (Figure
10D-F), induced by graphoepitaxial effect on M-plane
sapphire substrates, with diameters of several hundred
nanometers and lengths up to several millimeters.$^{172}$

### 3.1.3 Colloidal synthesis method

The successful appliance of the colloidal method on the
synthesis of perovskite quantum dots promotes it to the
fabrication of perovskite nanowires. The first colloidal
synthesis was based on an antisolvent precipitation
method. Zhu et al. dissolved PbX$_2$, MAX, and long-chain
CH$_3$(CH$_2$)$_2$NH$_3$X (X = Cl/Br/I) in a polar solvent (such
as ACN) and added the mixture into a solvent with lower
polarity (such as toluene), obtaining perovskite nano-
wires with precise control (Figure 10G).$^{199}$ When
switching to inorganic nanowires, representative works
employing the hot-injection method were performed by
Zhang et al.$^{190,192}$ Through injecting the cesium preci-
sor into the PbX$_2$ solution in the presence of oleylamine
and oleic acid at 150°C-250°C, they demonstrated the
fabrication of inorganic CsPbX$_3$ nanowires for the first
time (Figure 10H-M)$^{190}$ and controlled the compositions
and diameters in their subsequent work, enabling these
nanowires potential candidates for optoelectrical applica-
tions.$^{191,192}$ Afterward, colloid synthesis methods were
further investigated with more precise control. For
instance, Imran et al. prepared size-tunable CsPbBr$_3$
nanowires by introducing carboxylic acids with short
aliphatic chains (Figure 10N-P).$^{200}$ High PL quantum
yield up to 77% and color tunability from blue to green
were both obtained in these colloidal synthesized
nanowires.

### 3.1.4 Templated synthesis method

Using a template that confines the precursor to form the
desired structures seems to be straightforward. Ashley
et al. fabricated MAPbI$_3$ nanowires by selecting an AAO
membrane as the template (Figure 11A).$^{202}$ They drop-
cast perovskite precursor into the AAO pores and
followed with an annealing process to enable the forma-
tion. One obvious advantage here is the amenable diame-
ter control by selecting varisized AAO templates. In their
demonstration, MAPbI$_3$ nanowires with diameters rang-
ing from 50 to 200 nm, with a dispersity less than 10%
were synthesized readily. Later, Waleed et al. combined
the vapor-phase process with this template confinement
method, fabricating lead-free and inorganic perovskite
nanowires with a start from pure metals (Figure 11B).$^{203,205}$ To be
specific, AAO templates with double-sided pores. Then a reduced
pressure by a syringe was applied to enable the precursor
to fill in the pores of the template and extrude out on the
Transfer of the template onto glass spacers positioned on a hot plate would remove the solvent residue and promote the final formation of MAPbBr$_3$ nanowires (Figure 11E-G).

### 3.2 Applications of 1D metal halide perovskites

#### 3.2.1 Lasers

Anisotropic nanowires can serve as a waveguide along the axial direction, and the two end facets can form a Fabry-Perot cavity for optical amplification. Therefore, the single-crystalline perovskite nanowires with ideal facets are good candidates for the optically pumped lasers. The first lead halide perovskite nanowire-based laser was demonstrated by Zhu et al. (Figure 12A) from a room-temperature solution method, showing wavelength-tunable lasing with very low thresholds (220 nJ cm$^{-2}$) and a high-quality factor (Q ~ 3600) (Figure 12B). The further analysis estimated that the lasing quantum yield approaches 100% due to little charge carrier trapping in these nanowires. Using a similar solution method, nanowire lasers based on FAPbI$_3$ and their stabilized alloys were proposed by the same group (Figure 12C). The lasers exhibited durable lasing under...
FIGURE 12  Legend on next page.
$10^8$ shots of sustained illumination of pulsed laser excitation, substantially exceeding the stability of MAPbI$_3$ ($10^7$ shots) (Figure 12D). In addition to the solution process, vapor-phase synthesized nanowires were also suitable for nanolasers. The optically pumped MAPbI$_3$ nanowire lasers exhibited a wavelength of 777 nm, a threshold of 11 μJ cm$^{-2}$, and a quality factor of 405 (Figure 12E-G). In consideration of the stability issue, Eaton et al. first moved their eyesight onto inorganic CsPbX$_3$ nanowire-based nanolasers (Figure 12H). Compared to the organic counterparts, the inorganic metal halide nanowires showed robust property without sacrificing high emitting performance (Figure 12I). Low lasing threshold, high-quality factors, and robust stability under ambient conditions render the inorganic nanowires a promising platform for nanophotonic integrity.

### 3.2.2 | Solar cells

Due to the enhanced mechanical property and better conduction in specific directions, perovskite nanowires are also explored as absorber in solar cells. Park et al. first incorporated MAPbI$_3$ nanowires into the solar cell (Figure 13A) and investigated its optical and electrical properties. Compared to the nano-cubic counterparts, higher lateral conductivity was observed in nanowires, revealing a better connecting pathway. Time-resolved fluorescence spectroscopy confirmed that hole extraction from the nanowires was more efficient than that in the bulk case, mainly due to the better contact with hole transport materials from increased surface area. As a result, an improved PV performance with the best PCE of 14.71% was proved in nanowire-based solar cells (Figure 13B). Since then, a series of solar cells based on MAPbI$_3$ perovskite nanowires have emerged with modified fabrication processes (Figure 13C). A PCE of 18.83% with long-term stability was achieved through an integrated approach by Chang et al. (Figure 13D). In 2017, Kuang et al. fabricated solar cells based on CsPbX$_3$ nanowires with enhanced thermal and humidity stability compared to organic counterparts. The CsPbI$_3$ and CsPbBr$_3$ nanowire-based solar cells yielded the PCEs of 0.11% and 1.21%, respectively (Figure 13E). An impressive work was done in lead-free perovskites where Chen et al. synthesized high-quality CsSnX$_3$ (X = Cl/Br/I) nanorods for solar cell absorbers (Figure 13F). A PCE up to 12.96% under AM 1.5G has been achieved, revealing the potential of Sn-based perovskite nanorods in solar cell applications (Figure 13G). A summary of the key parameters of solar cells based on 1D perovskites is exhibited in Table 1.

### 3.2.3 | Light-emitting diodes

In 2015, through a solution method, Wong et al. successfully synthesized MAPbBr$_3$ perovskite nanorod arrays (Figure 14A), which were further converted into MAPbI$_3$ nanorods by an anion exchange reaction. Both types of nanorod arrays were applied as the active layer in LED devices (Figure 14B) and exhibited electroluminescent at room temperature (Figure 14C). Compared to thin films, the vertically oriented nanorod arrays offers several advantages, such as large active surface area, high carrier injection efficiency, and improved strain relaxation from thermal expansion. In their work, the MAPbBr$_3$ nanorod-based LED showed green EL at 532 nm with a full width at half maximum (FWHM) of 26 nm (Figure 14D) and the converted MAPbI$_3$ arrays showed infrared EL at 782 with an FWHM of 41 nm. This work demonstrates the potential of large-scale nanorod fabrication in LED applications.

### 3.2.4 | Photodetectors

In 2014, Horvath did the pioneering work of perovskite nanowire-based detectors (Figure 15A). Although the responsibility of this detector is 5 mA W$^{-1}$, 4 orders of magnitude smaller than that of state-of-art
detectors made from monolayer graphene, the response times (rise and decay times) were within 500 μs, ~10^4 faster than that of graphene-based detectors (Figure 15B). The photocurrent-dark current ratio and EQE at low voltages (<0.5 V) both showed superior performance than that based on their nanoparticle form, mainly arising from the reduced grain boundaries, which permit smooth carrier flowing channels in transport. In addition to these merits, enhanced absorption and mechanical integrity are other outstanding advantages. Zhu et al. demonstrated a MAPbI₃ nanowire-based photodetector on a flexible substrate from a post-solution treatment, revealing a 10% increase in absorption and enhanced mechanical property compared to thin-film based one (Figure 15C). Utilizing the morphological anisotropy of nanowires, Gao et al. demonstrated a photodetector with high polarization sensitivity and detectivity (2 × 10^13 Jones) for the first time. Considering the instability issues, several groups moved interests onto the inorganic counterparts. Waleed et al. used the AAO templates to fabricate CsPbI₃ nanowire-based photodetector, showing high stability when stored in organic polar solvents for 30 days.
thin CsPbBr$_3$-nanowires based photodetector, showing a sensitive photoresponse (Figure 15D). For practical spatial image applications, individual photodetectors should be integrated into arrays for graphic detection. Deng et al. demonstrated photodetector arrays for image mapping by synthesizing perovskite networks on poly(ethylene terephthalate) substrates. These arrays consisted of 49 individual detectors and could obtain a clear mapping of light source (Figure 15E). In the later work, Gu et al. increased the number of pixels to 1024 in each image sensor using well-aligned nanowires by a templated method discussed above (Figure 15F). The still images and videos could be well captured by these high-resolution nanowire arrays (Figure 15G). For further comparison, we summarize the key parameters of photodetectors based on 1D perovskites in Table 3.

4 | 0D METAL HALIDE PEROVSKITES

4.1 | Synthesis methods

4.1.1 | Ligand-assisted precipitation method

In 2014, for the first time, Schmidt et al. synthesized MAPbBr$_3$ nanocrystals (Figure 16A) by reacting the mixture of MABr and a long-chain alkyl ammonium bromide with PbBr$_2$ in the presence of oleic acid and octadecene. The nanoparticles were then precipitated by the addition of acetone and centrifugation. The as-synthesized nanoparticles exhibited diameters of ~6 nm and a strong PL intensity around 525 nm. Later, this method was adopted by several groups with further modification. For example, Zhang et al. produced brightly luminescent MAPbBr$_3$ nanocrystals with absolute PLQY up to 70% by the incorporation of n-octylamine and oleic acid as ligands (Figure 16B-D). The nanocrystals show an average size of 3.3 nm and binding energy to ~350 meV. Wei et al. synthesized perovskite nanocrystals by a homogeneous reaction in various nonpolar organic solvents (Figure 16E-G). Notably, this approach could be conducted in the open air and further extended to a gram level.

4.1.2 | Hot-injection method

In addition to ligand-assisted precipitation, hot-injection is another efficient method to synthesize monodisperse perovskite nanocrystals. Inorganic CsPbX$_3$ nanocrystals were achieved (Figure 17A-C) by the injection of cesium oleate into a mixed solution of PbX$_2$, oleic acid, and oleylamine in a high boiling solvent (octadecene) at
The synthesized nanocrystals showed stable, narrow, and broadly tunable photoluminescence with a quantum yield of 50%-90%. Subsequently, a low-temperature, partial/complete anion-exchange in CsPbX₃ nanocrystals was demonstrated by the same group (Figure 17D). The emission could cover the visible spectral region (410-700 nm) by reacting with suitable reagents in the precursors (Figure 17E). An inter-nanocrystal anion-exchange was further proposed, which could achieve CsPbClₓBr₃₋ₓ or CsPbBrₓI₃₋ₓ compositions by readily mixing CsPbCl₃, CsPbBr₃, and CsPbI₃ nanocrystals in proper ratios (Figure 17F).

### 4.1.3 Template-assisted method

Similar to 2D or 1D nanostructure fabrication, the template-assisted method is also suitable for perovskite nanocrystal synthesis. Kojima et al. demonstrated the MAPbBr₃ nanocrystal synthesis using a mesoporous alumina oxide in 2012.
The MAPbBr₃ nanocrystals were formed on porous Al₂O₃ film due to a rapid self-organized process after the dry of solvents. In 2015, Longo et al. utilized Al₂O₃ nanocrystals, with which MABr and PbBr₂ were mixed, to prepare perovskite nanocrystals with high PLQY. Spin-coating the mixture on a glass/quartz substrate and annealing the sample, the perovskite nanocrystals were formed with Al₂O₃ particles surrounding. The dimensions of perovskite nanocrystals were precisely governed by the sizes and concentrations of alumina nanoparticles. In addition, porous silica could also be used as templates. Malgras (Figure 18B-D) and Dirin et al. (Figure 18E-F) proposed a similar approach that they infiltrated perovskite solution into mesoporous silica followed by drying, synthesizing desired perovskite nanoparticles by the confinement of templates. Size distributions could be adjusted by the pores of silica to even 3.3 nm without sacrificing the high luminescent efficiency.

**4.2 | Applications**

**4.2.1 | Solar cells**

The pioneering work by Mayasiki in 2009 successfully demonstrated a perovskite nanocrystal-based solar cell,
exhibiting a PCE of 3.8% (Figure 19A). The performance was further improved by the Park group to 6.54% (Figure 19B-E), a record efficiency among perovskite nanocrystal-based PV devices. The research focus then moves onto inorganic counterparts like CsPbI$_3$ quantum dots owing to the consideration of tandem devices. Swarnkar et al. in 2016 developed a novel process to purify the as-formed quantum dots by the selection of methyl acetate, an antisolvent that removes excess unreacted reagents. The stability was significantly enhanced for the purified sample, which was stable in the cubic phase for months (Figure 19F). Solar cells based on these stable quantum dots showed an impressive PCE exceeding 10%, with a high open-circuit voltage up to 1.23 V. Further investigation, like utilizing AX salts like FAI to tune the coupling between perovskite quantum dots and increase charge transport properties between quantum dots arrays, boosted a record efficiency of quantum dots-based solar cell up to 13.4% (Figure 19H-J). A summary of the performance of perovskite nanocrystal-based solar cells is listed in Table 1.

4.2.2 | LEDs

High binding energy, strong PLQY together with tunable color gamut made perovskite quantum dots rather promising for LED fabrication. Song et al. used inorganic CsPbX$_3$ quantum dots as emitters in LEDs for the first time (Figure 20A). It showed a wide color tunability from blue to orange by simply changing the anionic composition, but a low luminance and EQE accompanied simultaneously (Figure 20B). The moderate performance...
is possibly attributed to the excess long ligand on quantum dots’ surface that hampered the efficient carrier transporting. Replacing these long ligands with shorter one would address this issue effectively. Pan et al. realized efficient LEDs based on CsPbX₃ quantum dots, which were capped by relatively short ligand (eg, di-dodecyl dimethyl ammonium bromide) (Figure 20C), and achieved much improved EQE (1.9% for the blue, and 3.0% for the green) (Figure 20D-E). Li et al. achieved a 50-fold EQE enhancement by balancing surface passivation and carrier injection of perovskite quantum dots (Figure 20F). An EQE up to 6.27% in the CsPbBr₃ nanocrystal-based LED has been obtained by precisely controlling the ligand density on the surface. Besides, the current efficiency was 30-fold improved up to 13.3 cd A⁻¹, as well (Figure 20G). In addition to these solutions, other strategies like surface engineering and so on were also proposed to address the remaining problem,
significantly accelerating the development of nanocrystals based LEDs.\textsuperscript{150,151,155-158,228,229} Recently, some types of 0D perovskites were demonstrated to possess broadband emission, which are promising candidates for the applications of down-conversion white LEDs.\textsuperscript{50,230-233} Zhou et al. replaced the element lead by tin and selected different ligands, demonstrating 0D perovskites with tunable broad emission.\textsuperscript{230} Through the manipulation of locally collective hydrogen bonding, Cui et al. successfully tailored the assembling behavior and synthesized 0D perovskite single crystal with “warm” white emission and enhanced PL efficiency.\textsuperscript{231} By combining the hybrid
with the commercial phosphor in various ratios, Worku et al. fabricated UV-pumped white LEDs with tunable color gamut, from “cold” to “warm” white. More detailed parameters of LEDs based on perovskite nanocrystals are listed in Table 2.

### 4.2.3 Lasers

In 2015, Yakunin demonstrated the spontaneous emission and lasing in blue and green spectral regions from ~10 nm monodispersed CsPbX_3 nanocrystals. Low pump thresholds down to 5 ± 1 μJ cm⁻², together with high values of a modal net gain of at least 450 ± 30 cm⁻¹, were demonstrated in this system (Figure 21A). Two lasing modes were observed. One was the whispering-gallery-mode where silica microspheres as high-finesse resonators were coated with CsPbX_3 nanocrystals and the other was random lasing in films of CsPbX_3 nanocrystals. Later work by Wang et al. demonstrated a CsPbX_3 nanocrystal-based laser, with a low threshold of 22 μJ cm⁻², wide color tunability, and good stability (Figure 21B). Based on this, the same group investigated the manifested nonlinear absorption and multiphoton pumped stimulated emission from 9 nm-sized CsPbBr_3 nanocrystals (Figure 21C). Low-threshold and tunable frequency-
upconverted stimulated emission by two-photon absorption and green stimulated emission by three-photon were both obtained from the CsPbCl₃Br₃₋ₓ nanocrystals, providing promising opportunities in nonlinear photonics (Figure 21D).  

Figure 21  A, Photoluminescence (PL) emissions of a microsphere resonator (15 μm in diameter, covered by a film of CsPbBr₃ nanocrystals) at the excitation intensities around the lasing threshold. The inset is a schematic of whispering-gallery-mode (WGM) lasing in a sphere. Reproduced with permission. Copyright 2015 Nature Publishing Group. B, Stimulated emission from small-sized CsPbX₃ quantum dots with different compositions. Reproduced with permission. Copyright 2015 Wiley-VCH. C, PL decays of CsPbBr₃ nanocrystals based on one-, two-, and three-photon excitation. The inset is an illustration of the whole process of one-, two-, and three-photon excited PL. D, Photograph of the stripe pumping configuration. A strong green PL can be seen by the pump of 800 nm laser. Reproduced with permission. Copyright 2016 American Chemical Society

Although 3D perovskite has been investigated intensively, the exploration of low-dimensional perovskites has not caught the pace of 3D counterparts in multiple aspects. It can be expected that advantages arising from low dimensionality can be further magnified both fundamentally and practically.

5 | OUTLOOK

As one of the most valuable merits with reduced dimensionality, size and dimensional control for various bandgaps attract tremendous attention. Nowadays, although some groups can manipulate the perovskites with size and shape control to some degree, most synthesis methods for low-dimensional perovskites are trial-and-error, without a precise regulation. With the emerging machine learning techniques recently, Lu et al. can predict enormous perovskite structures and even material stability, according to the former database. We are inquisitive whether this approach can be utilized as the guidelines for the synthesis of...
perovskites with accurate structures and dimensions we desire. Based on these, more explorations of in-depth physical mechanism and wide applications will be duly concomitant.

5.2 Understanding of the physics in low-dimensional perovskites

Since tremendous optoelectronic applications have been demonstrated, the investigations focusing on fundamental properties of low-dimensional perovskites have not attracted much attention. With the reduced dimensions, some inherent natures like band structure and photon transport will behave differently. For example, reduced thermal conductance from the enhanced boundary scattering, together with the improved Seebeck coefficient from the modified energy band, makes low-dimensional perovskites potential materials for thermoelectrics.\(^{242-246}\) Recently, Wang et al. have investigated the cation dynamics governed by thermal properties in different types of perovskite nanowires.\(^{244}\) However, the study on this aspect is limited and more efforts should be devoted to further exploration. In addition, the low dimensionality could also bring about confined charge transport in the selected directions, leading to unique electrical properties such as 2D electron gas, which is the basis for field-effect devices.\(^{247,248}\) However, these fundamental investigations rather lag behind the application and is supposed to draw more attention in the near future.

5.3 Exploration of new applications

In addition to the applications in solar cells, LEDs, lasers, and photodetectors, metal halide perovskites may possess other suitable uses. For example, Liao et al. have demonstrated ferroelectricity in bulk 3D perovskite.\(^{249}\) It is expected that the strong quantum and dielectric confinements of nanostructures may bring up much-enhanced ferroelectricity, which calls for more systematic investigations in low-dimensional nanoplatelets or nanowires.

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CONFLICT OF INTEREST

The authors declare no potential conflict of interest.

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