Review article

Xiao Han, Yongshen Zheng, Siqian Chai, Songhua Chen* and Jialiang Xu*

2D organic-inorganic hybrid perovskite materials for nonlinear optics

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Abstract: Two-dimensional (2D) organic-inorganic hybrid perovskites feature characteristics of inherent quantum-well structures and intriguing optoelectronic properties, and have therefore attracted enormous research attention for their optical applications in light emitting, sensing, modulation, and telecommunication devices. The low-cost and solution-processed fabrications as well as alternative organic spacer cations endue 2D hybrid perovskites with higher tunability in optical and photonic applications. In particular, they demonstrate distinguished nonlinear optical characters such as second-harmonic generation (SHG), two-photon absorption (2PA), and saturable absorption (SA) under the excitation of laser pulses. Here, we discuss the construction of the various sorts of 2D hybrid perovskites with different structural features. We have also highlighted some representative properties and applications of these 2D hybrid perovskites in both linear and nonlinear optical regimes.

Keywords: 2D hybrid perovskites; quantum-well structure; structure tunability; nonlinear optics.

1 Introduction

Since the single-atom layered graphene came to light in 2004 [1], two-dimensional (2D) materials have been in the state of booming development and rapid advances in the past decade [2]. The subsequent new 2D materials such as the transition metal chalcogenides (TMDs) [3–5], graphdiyne (GD) [6–11], hexagonal boron nitride (h-BN) [12, 13], and black phosphorus (BP) [14, 15] have been implemented for applications in optoelectronics [16], photonics [17–20], catalysis [21], energy conversion, and storage materials [22, 23], on account of their autologous admirable chemistry and physics characteristics. Moreover, these 2D materials are easily manufactured into thin films or nanocrystals, and are widely applied in nanophotonics as they feature the advantages of large surface areas [24], enhanced robustness [25] and mechanical flexibility [26], superior surface sensitivity to circumstances [27], fascinating quantum effects in heterostructures [28, 29], and feasible stacking modes by van der Waals forces [30].

Perovskites, especially the organic-inorganic hybrid halide perovskites, are regarded as high-performance semiconductors in virtue of their low fabrication costs and outstanding properties [31]. The most dramatic representation of perovskite materials is their emergence as one of the most prominent photovoltaic materials [32, 33], and have therefore obtained remarkable excitements in dramatically improving the photoelectric conversion efficiency over the last 10 years [34]. By shrinking down the dimension of three-dimensional (3D) hybrid perovskites to 2D, it brings about unique properties such as the large exciton binding energy (>100 meV), long carrier diffusion length, strong light harvesting capability, controllable charge-carrier mobility, and efficient photoluminescence intensity [35, 36]. In their structures, the synergistic combination of the insertion of heavy atoms and the rigid blocks of the inorganic [BX₆] octahedrons promotes the implementation of room-temperature phosphorescence (RTP) and thermally activated delayed fluorescence (TADF) luminescent materials [37]. Moreover, the substitutable organic ligands and metal cations provide the possibilities of flexible crystal structure, elevated resistance, adjustable bandgaps, narrowband, or broadband emission.

Nonlinear optics (NLO) deals with the strong interaction of matter with the intense lights, and is of key importance for modern technologies such as the all-optical...
2 The structure of 2D perovskites

The first discovered perovskite, CaTiO$_3$, affiliates to a representative 3D perovskite system described by the general formula ABX$_3$. Typically, A represents a small organic or inorganic cation, B denotes a transition metal cation (such as Pb$^+$, Sn$^+$ or Ag$^+$), and X refers to a halogen anion (Cl$^-$, Br$^-$ and I$^-$), with the foundation of corner-sharing [BX$_6$] octahedron [73, 74]. Generally, the construction of ABX$_3$ perovskites should stick to the Goldschmidt tolerance factor, which determines the constraint of the A cation radius of 2.6 Å, aiming to maintain a stable and rigid 3D skeleton [75, 76]. Further explorations reveal that a fine change in the composition of A cation will lead to a variety of structures, morphologies and even dimensions of the perovskite materials [77]. With the Goldschmidt tolerance factor $t > 1$, the initial 3D scaffold is tough to shape. Instead, it is transformed to the low-dimensional (2D, 1D, 0D) perovskites.

Conceptually, the 2D hybrid perovskites with the recognized formula R$_n$A$_{n-1}$B$_n$X$_{3n+1}$ (R stands for an additional bulky organic cation) [78] can be deemed as the excised sub-structure stemming from the primary 3D matrix. Thus, the 2D layered perovskite can be categorized into the (100), (110) and (111) derivatives by slicing the 3D frame along different crystallographic orientations (Figure 1) [79]. Conversely, the conversion from the pure 2D perovskite to quasi-2D perovskite and then to 3D perovskites will be realized by increasing the number of perovskite layers (the value of n) (Figure 2) [80]. As the (100) 2D perovskite derivatives dominate the 2D halide perovskite family [81] herein, this section will be divided into (100) perovskite derivatives and other perovskite derivatives including the (110) and (111) 2D perovskites.

2.1 (100) perovskite derivatives

Structurally, the (100) perovskite derivatives can be mainly subdivided into R-P (Ruddlesden-Popper) phase [82, 83], D-J (Dion-Jacobson) phase [84–86], and ACI (alternating...
cation in the interlayer space) phase [87, 88] layered perovskites, characterized by the general formulation of $A'B_n^{n-1}B_nX_n^{n+1}$, $A''A'B_n^{n-1}B_nX_n^{n+1}$, and $A'B_n^{n-1}B_nX_n^{n+1}$, respectively. Variations between these three types of 2D perovskites are primarily reflected in the stacking modes of the inorganic components. In contrast to the R-P phase and the ACI phase, the D-J phase adopts a more uniform stacking mode for the neighboring inorganic bilayers in the $(a, b)$ layer plane, exhibiting the $(0, 0)$ in-plane displacement [89]. In the case of the R-P phase and ACI phase, a relatively staggered configuration can be observed, showing $(1/2, 1/2)$ and partial $(1/2, 0)$ displacements, respectively [86]. For the R-P phase perovskite, a pair of monovalent spacer cations is intercalated within the interlayer of each octahedral cell (Figure 3), while it requires a sole bivalent spacer cation for the D-J phase counterparts. Consequently, the tiny distinction leads to the shorter interlayer distances for the D-J and ACI perovskites. In R-P perovskites, the inorganic cubic layers stack more flexibly and freely, resulting in the weaker intermolecular interplay. In addition, the delicate alterations in the interlayer spacing can dramatically affect the optoelectronic properties of the perovskites. For instance, Iwan et al. reported tin perovskites based on the symmetrical Bn (benzimidazolium) and Bdi (benzodimidazolium) cations [90]. The two imidazole rings in Bdi$^{2+}$ cations interacting with the upper and lower layers simultaneously (Figure 4A) compressed the layer spacing of Bn$_2$SnI$_4$ (13.95 Å) into 10.59 Å for BdiSnI$_4$ (Figure 4B). Such an alteration in the interlayer spacing resulted in the preferential crystal growth along the (001) orientation and the lower conductivity for Bn$_2$MI$_4$ compared to that of the BdiMI$_4$ analogs. Similarly, Li et al. presented two 2D D-J phase halide perovskites (4AMPY)(MA)$_{n-1}$PbI$_n$ and (3AMPY)(MA)$_{n-1}$PbI$_n$ (MA = methylammonium, 4AMPY = 4-(aminomethyl)pyridinium, 3AMPY = 3-(aminomethyl)pyridinium). The shorter distance in layer spacing gave rise to the narrower bandgap
for the (3AMPY)(MA)$_n$Pb$_{1+n}$ perovskite and a smaller exciton binding energy ($E_b$) for the aromatic system by the easy separation of electron-hole pairing in the quantum-well structures [91].

Apart from the layer distance, the number of layers and the distortion of perovskite lattice are also closely related to their optoelectronic properties. Compared to the 3D structured perovskites, the low-dimensional 2D or quasi-2D perovskites feature larger $E_g$, higher $E_b$, and improved photoluminescence quantum yields (PLQYs) owing to the quantum confinement effect in the 2D plane and surface passivation [92–94]. When $n \geq 2$, the gradually assembled inorganic octahedron layers induce to form the as-called “well” layers with the increasing value of $n$ [95]. In the ACI-type perovskite (C(NH$_2$)$_3$)(CH$_3$NH$_3$)$_n$Pb$_{1+n}$, it showcases a monotonic optical gap through changing the layer thickness in the same system [88]. Interestingly, when the number of layers is odd ($n=1, 3$), this ACI perovskite belongs to a centrosymmetric Imma space group, whereas when the number is even ($n=2$), the architecture adapts to a noncentrosymmetric (NCS) Bmm2 space group (Figure 5). This alteration originates from the change of the crystal symmetry element, in which a mirror plane is displayed for even numbers while the plane is substituted by a glide plane for odd numbers. Similarly, Yuan et al. adopted an innovative channel to tune the emitting colors by manipulating the layer thickness $n$ and the organic cations in nanoscale layered hybrid halide perovskite [96]. The PL luminescence exhibited a red-shift from deep-blue to green with increasing the $n$ from 1 to infinity by the one-pot reverse micelle method.

Generally, the distortion effect can be estimated by the B-X-B octahedral angle, and the larger angle usually corresponds to the slighter distortion of crystal skeleton [89, 97]. The structure deformation in perovskite lattices has a smaller impact on the system than that of the interlayer spacing [89], but it still plays an invaluable role in tuning the properties of the perovskite materials. For instance, the self-trapped excitons (STEs) resulting from the transient lattice distortion lead to the strong Stokes
Figure 4: Effect of interlayer spacing on perovskites. Structural drawings of the 2D perovskites [benzimidazolium]$_2$SnI$_4$ (A) and [benzodiimidazolium]SnI$_4$ (B) perpendicular to the stacking direction. The $d$-spacing between the single perovskite sheets indicated. The corresponding diffraction patterns of the 2D perovskites spin-coated on glass substrates are shown underneath. Reprinted from Ref. [90] with permission from the Wiley-VCH.

Figure 5: Effect of layer number on (GA)$(MA)_{nPb_{n+1}}I_{3n+1}$ perovskite structures. View of the unit cells of the (GA)$(MA)_{nPb_{n+1}}I_{3n+1}$ ($n=1$–$3$) perovskites along (A) the crystallographic $b$-axis and (B) the crystallographic $a$-axis highlighting the ordered crystal packing of the GA and MA cations between the perovskite layers. Reprinted from Ref. [88] with permission from the American Chemical Society.
shifts and ultra-band emission [97–99]. Recently, Jung fabricated (BZA)_2PbBr_{4-x}Cl_x (BZA = benzylammonium and x = 0, 1.5, 2, 3, 3.5, 4) perovskite series for tunable solid-state light emitting [100]. The perovskites (BZA)_2PbBr_4 and (BZA)_2PbCl_4 displayed narrow blue and glaucous emission, respectively. Comparing to the structural data in different inorganic blocks, the Pb-Br-Pb bond angles of the adjacent octahedra were nearly identical (149.9° and 150.0°) (Figure 6C) while the Pb-Cl-Pb bond angles varied sharply (142.2° and 154.4°) (Figure 6D). Therefore, the larger deformation of (BZA)_2PbCl_4 brought about a broadband emission. Analogously, Zhang et al. reported the broadband emission from a hybrid perovskite (C_6H_5C_2H_4NH_3)_2PbBr_4 through the structure transitions under different pressures (Figure 7) [101]. The bathochromic shift and reduced photoluminescent intensity were observed upon the increased pressure.

Figure 6: Effect of distortion on (BZA)_2PbBr_4 perovskite. (A) Blue-light emission from (BZA)_2PbBr_4 powdered polycrystalline sample and white-light emission from the (BZA)_2PbBr_{4-x}Cl_x (x = 1.5, 2, 3, 3.5, 4) perovskite series under ultraviolet (UV) excitation at λ_{ex} = 365 or 254 nm. (B) Diffuse reflectance spectra and band gaps of the solid powder of the (BZA)_2PbBr_{4-x}Cl_x perovskite (x = 4, 3.5, 3, 2, 1.5, 0) series. Structural geometry of (C) (BZA)_2PbBr_4 and (D) (BZA)_2PbCl_4. Bond distances of (E) Pb-Br and (F) Pb-Cl for PbBr_6^2− and PbCl_6^2− octahedra, respectively. Reprinted from Ref. [100] with permission from the American Chemical Society.
which possessed considerable potential for photodetector in ultrahigh pressure environments.

### 2.2 Other perovskite derivatives

The (110)-oriented perovskite derivatives are relatively rare among the three types of 2D perovskite derivatives, as very few organic cations can stabilize this 2D framework. Nevertheless, the major hydrogen-bonding interactions in (110)-oriented derivatives can not only stabilize the 2D perovskite blocks, but also affect the growth of the structure [102]. The special stack of organic cations in the pockets of malleable inorganic skeleton drives the formation of the distorted structure of (110)-oriented perovskites. Practically, the (110)-oriented family are the most crooked perovskite derivatives among the 2D perovskites, marked by roof-like layers with the general formula of \( A'_2 A_{x-y} B_x X_{3-y} \) [103]. In terms of the “ridge length” of the roof-like octahedral lattices, the series of (110)-oriented perovskites can be classed into three series, namely the “2×2”, “3×3”, and “4×4” (Figure 8) [104, 105]. Certainly, the highly twisted structure of (110)-oriented perovskites endows them with broadband emission at room temperature due to the STE effect [106–108].

The (111)-oriented perovskite structures, expressed by the formula \( A'_2 A_{x-y} B_x X_{3-y} \), can be considered as the split of the 3D matrix crystal cell along the body diagonal, which results in the initiative defect in the M-sites [89, 109]. The \( A'_2 A_{x-y} B_x X_{3-y} \) family consists of monovalent
cations (R-NH₃⁺, Cs⁺, Rb⁺) and group VA elements B (As³⁺, Sb³⁺, Bi³⁺). Meanwhile, it spontaneously forms 2D corner-sharing layered perovskites \((k=2)\) or 0D face-sharing dimer clusters \((k=1)\) in order to stabilize the stereoscopic configuration of \((B₂X₉)³⁻\) (Figure 9) and realize the charge balance \([110, 111]\). It is noteworthy that, when \(k>2\), the B cation participating in the construction of \(A'ₐA₂Xₙ₋₁BₙXₙ⁺₁\) should be in a fractional valence state or a mixture of different valence states. Recently, Vargas et al. synthesized a \((111)\)-oriented 2D perovskite \(Cs₄CuI₃SbⅢClII\) with \(k=3\) \([112]\), and corner-sharing \(CuCl₆\) and \(SbCl₆\) unit cells composed the main framework collectively (Figure 10).

Both the flexible structures \([113]\) and excellent properties emerge from the controllable syntheses of 2D perovskites, which are determined by their inherent weak ionic bondings \([114]\). The main fabrication methods of 2D hybrid perovskites could be divided into solution methods and vapor methods \([115]\). In general, the advantages of solution methods include the economy as well as the multiple morphologies of perovskites acquired facilely by changing the solution system. In 2015, Dou et al. fabricated ultra-thin 2D hybrid perovskites of \((C₄H₉NH₃)₂PbBr₄\) through solution-crystal growth \([36]\). With the assistance of the ternary solvent system \([dimethylformamide (DMF), chlorobenzene, and acetonitrile]\), uniform 2D sheets crystallized on the substrate with the minimum thickness approximate to 1.6 nm. Wang et al. investigated the effect of the concentration of Cl incorporation to the morphology, crystal phase, and optical property of \((BA)₂SnI₄Clₓ \left( BA=n-CH₂CH₂CH₃NH₃ \right) \) perovskites \([116]\). The morphology of 2D perovskite converted from plates to needles upon increasing the Cl dosage. Meanwhile, the emission peak of the samples exhibited a redshift and the phase transition temperatures varied dramatically with a higher Cl ratio. The vapor methods could be categorized into chemical vapor deposition (CVD) \([117]\) and van der Waals epitaxy. Although vapor methods are usually costly and require higher temperature, they are appropriate for 2D perovskites with better crystallinity and higher purity. Chen et al. combined the solution method and CVD of \(CH₃NH₃Br\) to synthesize the 2D homologous perovskite \((BA)₂(MA)ₙ₋₁PbₙBrₙ⁺₁\) \([118]\). The resultant ultrathin and large-sized perovskites showed superior optoelectronic response and outstanding stability. Chen et al. reported high-quality \((C₄H₉NH₃)₂PbI₄\) flakes via van der Waals epitaxy, and the crystal thickness as well as the electron-phonon coupling strength diminished due to the van der Waals interaction \([119]\).

## 3 Optical properties and applications

Owing to the insertion of larger organic cations, the prototypical structural alignments of 3D perovskites are disturbed \([120]\). Consequently, the initial inorganic motifs are sandwiched by protruding bilayers of organic cations \([121]\), which brings about the higher carrier mobility and tunable bandgap in inorganic layers \([122, 123]\). Thus, the 2D hybrid organic-inorganic perovskites exhibit much lower dielectric coefficient and stronger exciton binding energy as compared to the 3D homologs \([114]\). Furthermore, the scalability and replaceability of organic components in the solution process also endow the 2D perovskites with diverse and fascinating optical properties as well as super extensive applications \([94, 124, 125]\).
3.1 Linear optical properties of 2D perovskites

Photoluminescence [126] at the room temperature is an important photophysical phenomenon for 2D layered perovskites, and the essence is the radiative recombination of the excitons [127]. The self-location of excitons enhances the Stokes shift and the wide emission range, making the 2D perovskites prevalent materials for applications in light-emitting diodes (LEDs) [128, 129], solar cells [130, 131], and photodetectors [132, 133].

In early 2014, Dohner et al. synthesized a series of 2D white-light emission layered perovskites (EDBE)[PbX₄] (EDBE = 2,2′-(ethylenedioxy)bis(ethylammonium); X = Cl, Br, and I) with improved photoluminescence quantum efficiencies (PLQEs) of up to 9% [134]. The constant and stable irradiation maintained for 3 months, and further studies on the crystal structures demonstrated that the lattice deformation stemming from the exciton coupling and the intrinsic self-trapping effect contributed to the successive and broad white-light emission [135, 136]. Based on this principle, a series of 2D hybrid perovskites, for instance, (C₆H₅C₂H₄NH₃)₂PbCl₄ [137], (CH₃CH₂NH₃)₄Pb₃Br₁₀₋ₓClₓ [138], (C₄H₉NH₃)₂PbCl₄ [139], and (3APr)PbX₄ (3APr = 3-amino-pyrrolidinium) [102], all exhibiting prominent white-light emission under ambient condition, have been designed and synthesized.

The long afterglow emitting materials, including TADF and RTP, have aroused intensive interest and have potential applications in the fields of sensors, storage and security domains [140]. In addition, the intersystem crossing (ISC) process for RTP and the reverse intersystem crossing (RISC) process for TADF emitters endow them with the privilege of reaching an internal quantum efficiency (IQE) up to 100% [141]. Zhou and Yan developed a cadmium (Cd)-based hybrid halide 2D perovskite, CdCl₂·4HP (4HP = 4-hydroxypyridine), with the characteristic D-π-A architectural design, which presented the delayed fluorescence emission at 416 nm with a long lifetime of 103.12 ms (Figure 11C and D) [37]. The rare deep-blue luminescence (Figure 11B) and high emissive efficiency (63.55%) have been ascribed to the quantum confinement effect, the suitable heavy-atom effect, and the rigid lamellar layers. Analogously, Hu et al. observed the phosphorescence of...
fresh 2D perovskite (PEA$_{1-x}$TTMA$_x$)$_2$PbBr$_4$ (PEA = phenethylammonium, TTMA = thieno[3,2-b] thiophene-2-methylammonium) with a long lifetime of 0.2 ms and a very high phosphorescence yield (11.2%) at room temperature [142]. The TTMA organic molecule emits no phosphorescence at room temperature because the transition from triplet state (T$_1$) to ground state (S$_0$) is forbidden [143]. However, when the TTMA organic molecule was inserted into the inorganic framework of perovskite, the energy harvested in the inorganic component transferred to TTMA, inducing the appearance of phosphorescence. Further studies implied that the employment of the host-guest system to the perovskite by mixed cation can effectively suppress the nonradiative recombination to improve the longevity and phosphorescence yield [144, 145].

The alternative organic spacer cations in perovskites can not only change the bandgap, emitting color [142], lifetime, stability [146], and efficiency [147], but also bring about the new optical properties. For example, when chiral organics are introduced into the perovskite scaffolds, the pristine geometrical centrosymmetry will be broken. As a result, distinctive optical response to oppositely signed circular dichroism (CD) and circularly polarized light (CPL) could be detected. In 2018, Yuan et al. reported an original NCS perovskite by incorporating chiral amines into the perovskite crystal structure [148]. The 2D stratiform perovskite (MPEA)$_{1.5}$PbBr$_{3.5}$(DMSO)$_{0.5}$ was fabricated by antisolvent vapor-assisted crystallization (AVC) with a mixed solvent system [antisolvent: CHCl$_3$, good solvent: DMF/dimethyl sulfoxide (DMSO)]. The crystallographic structure of the 2D perovskite demonstrated that the DMSO solvent molecules partially substituted Br intercalated between the partial edge sharing inorganic slab and coordinated with Pb$^{2+}$ (Figure 12A).

From the spin-coating films of R- and S-(MPEA)$_{1.5}$PbBr$_{3.5}$(DMSO)$_{0.5}$, both the R- and S- perovskite films exhibited intensive CD signal response at 325 and 405 nm springing from the Cotton effects of excitonic absorbance band (Figure 12C). Moreover, the nanowire crystals, grown by liquid diffusion in the identical ternary solvent system, subordinated to the same triclinic P1 space group. From the diffusive reflectance spectrum, the optical bandgap was calculated to be around 3.07 eV, meanwhile the perovskite nanowires showed the wide emission range.

Figure 12: Structures and linear optical properties of R- and S-(MPEA)$_{1.5}$PbBr$_{3.5}$(DMSO)$_{0.5}$ perovskites. (A) Crystallographic structure of the chiral perovskites as obtained from single crystal XRD measurements, showing the features of chirality, DMSO intercalation, and partial edge sharing. (B) Normalized DRS (diffusive reflectance spectrum) and fluorescence spectra of the as-prepared (R-MPEA)$_{1.5}$PbBr$_{3.5}$(DMSO)$_{0.5}$ nanowires. Excitation wavelength: 400 nm. (C) Normalized CD spectra of the films spin-coated from DMF solutions of the R- and S-(MPEA)$_{1.5}$PbBr$_{3.5}$(DMSO)$_{0.5}$ perovskite crystals. The average film thickness for both R- and S-(MPEA)$_{1.5}$PbBr$_{3.5}$(DMSO)$_{0.5}$ is ~350 nm. Reprinted from Ref. [148] with permission from the American Chemical Society.
including the entire visible region under the stimulation at 400 nm (Figure 12B). Emission of the nanowire crystals had a CIE (Commission International de l’Eclairage) coordinate of (0.40, 0.42), emitting the “warm” yellowish white light, whereupon it promised to be optical devices for LED or photo-communication.

In 2018, Long et al. reported the 3% spin-polarized photoluminescence in 2D chiral perovskites without ambient magnetic field [125], which could only be achieved in traditional 3D perovskites under an applied magnetic field of 5 T. The introduction of chiral ligands \((R-/S\)-methylbenzylammonium bromide\) in 2D perovskites \((n=2)\) presented appreciable chirality in CD spectra and efficient CPL emission. Moreover, the degree of polarization of racemate of perovskite enantiomers varied linearly with external magnetic field, realizing the spin control for achiral perovskites.

Recently, Wang et al. prepared the orange and needle-like chiral perovskite 
\[ \text{R/S-}\alpha-(\text{PEA})_2\text{PbI}_4 \]
through the facile aqueous synthesis pathway in 57% hydrogen iodide (HI) solution without annealing [149]. Comparing the emission intensities of left (\(\sigma^-\)) and right (\(\sigma^+\)) circularly polarized at approximately 500 nm, however, there are apparently unlike intensities for \(\sigma^-\) and right \(\sigma^+\) (Figure 13A and B), suggesting the efficient selective emission in this pair of chiral perovskite enantiomers. Further implementing the chiral perovskites into the CPL detection, it also displayed the outstanding repeatability and optical switch characteristics in Figure 13C, and the ultrahigh external quantum efficiency (close to 140%) was realized.

Except for the versatile luminescent materials, the 2D hybrid perovskites also exhibited absorbing properties in photodetection devices like other popular materials [Bi quantum dots (QDs) [150], Te nanosheets [151], Se nanosheets [152], tin sulfide (SnS) [153], and BP [154]]. The direct gap with high density of state in hybrid perovskites will enhance the interaction between light and matter [155]. Thus, they generally possess large responsivity [156], on/off current ratio [157], and the ultralow dark current [158]. For instance, Tan et al. prepared 2D perovskite \((\text{C}_2\text{H}_5\text{NH}_3)_2\text{PbBr}_4\) crystals for photodetection via solvent evaporation [159]. Covered with graphene film, the detector was demonstrated to exhibit much higher responsivity (2100 A/W) than other typical 2D materials. Analogously, Qian et al. reported microsheets of the Sn-based 2D perovskite \((\text{PEA})_2\text{Sn}_{x}\text{Br}_{x}\) \((x=1, 2, 3)\), and the largest photoreponsivity (3290 A/W) and detectivity \(2.06 \times 10^{11}\) Jones were observed for \((\text{PEA})_2\text{SnI}_4\) under 470 nm illumination [160]. Although the 2D hybrid perovskites are superior in the aspects of responsivity and detectivity, their effective spectral ranges are generally narrower than Bi QDs, Se nanosheets, SnS, or other 2D materials.

### 3.2 2D perovskites for nonlinear optics

The classical and emerging 2D materials, such as graphene, BP [161], SnS [162], and Se nanosheets [163], have been attempted for NLO applications recently. For example, the graphene is characterized by broadband and intensity-dependent NLO absorption, but the inherent symmetry in the original structure limits its second-order NLO application [164]. Resembling the graphene, BP is a mono-elemental 2D anisotropic material consisting of active phosphorus atoms [161, 165]. It usually exhibits its fascinating wideband third-NLO effects [for example, four-wave mixing and third harmonic generation (THG)] from the visible to the mid-infrared (IR) [18, 166] and size-dependent NLO phenomena [65]. Moreover, the NCS lattice structure [167] of BP enables it to be utilized in second-order NLO directly. The novel SnS layered material assumes extraordinary chemical and thermal stability in contrast to other 2D materials [168], along with tunable band gap and odd-even quantum confinement [169].

![Figure 13: Optical characteristics of R- and S-\(\alpha\)-(PEA)\(_2\)PbI\(_4\) perovskites.](image)

(A, B) Circularly polarized PL emission of \((S)-\alpha-(\text{PEA})_2\text{PbI}_4\) and \((R)-\alpha-(\text{PEA})_2\text{PbI}_4\) crystals. (C) Optical switching characteristic of the \((R)-\alpha-(\text{PEA})_2\text{PbI}_4\) device under a 520 nm monochromatic \(\sigma^-\) and \(\sigma^+\) illumination at a bias of \(-3\) V. Reprinted from Ref. [149] with permission from the American Chemical Society.
a result, few-layer SnS has been employed in all-optical information conversion, all-optical switching [162], and SA [170] due to its intriguing third-order NLO responses. In addition, theoretical investigations implied that the unique NCS \(C_{2x}\) (mm2) point group of SnS monolayer could offer its giant second-harmonic generation (SHG) susceptibility [171]. 2D trigonal Se nanosheets show extraordinary NLO properties derived from the bigger surface and size-dependent band gap [163], revealing the potential for saturable absorber and ultrafast photonics.

Comparing with the 2D materials mentioned earlier, the rich chemical and structural diversity of 2D hybrid perovskites endows them with multiple advantages for NLO applications [53]. The resultant multiple-quantum-well (MQW) construction of exciton will strengthen the NLO properties [172]. Besides, the lattice structures and morphologies of these layered 2D hybrid perovskite materials are abundant and tunable by using different pathways. High-quality and uniform 2D perovskite crystals could be obtained by solution or vapor pathways facilely [115], in comparison with the usually low yield [173], low quality [174], and strict preparation conditions [175, 176] in the processes of fabrication of other classical 2D materials. Moreover, the facile substitutability of organic cations in 2D hybrid perovskites provides convenient conditions for regulations of NLO processes. These tempting advantages drive the growth and development of 2D hybrid perovskites for NLO. However, the lower stability than graphene, SnS, and Se nanosheets is the main drawback and challenge for 2D hybrid perovskites. In short, the advent of 2D layered perovskites opens a new chapter for NLO thanks to their merits of low cost, facile preparation, tunable construction, well-defined morphology, and large NLO coefficient. In view of this, the recent advancements and applications of 2D perovskites for NLO are summarized in this section, and the second- and higher-order NLO properties of 2D perovskites will be discussed, respectively.

### 3.2.1 2D perovskites for second-order NLO

In 1961, Franken et al. observed SHG from crystalline quartz for the first time [177], and the special and intriguing phenomenon opened the prelude of NLO. After that, a plethora of NLO effects have been discovered with the emergence and rapid development of novel NLO materials. Even now, SHG is still a vital phenomenon in the NLO field [178–180]. Yet, the second-order NLO effect in centrosymmetric crystal class is forbidden on account of the nearly zero second-order nonlinear optical susceptibility in electric-dipole approximation [181, 182]. Thus, the quadratic NLO is limited in the NCS structures [183, 184] or the interface on the centrosymmetric structure.

It is uncommon for the majority of 2D perovskites to be second-order NLO activity due to the space structure symmetry. Wang et al. presented an efficient white-light emitting 2D hybrid perovskite (2meptH2)PbBr4 (2mept represents 2-methyl-1,5-diaminopentane) [185]. Besides the broadband emission range and high PLQY, it also exhibits SHG response under the 1064 nm laser [neodymium-doped yttrium aluminum garnet (Nd:YAG)] excitation (Table 1). Single crystal X-ray powder diffraction (XRD) analysis demonstrated that this perovskite was stacked in the polar Cc (No. 9) space group derived from the crumple of contiguous inorganic octahedron, which also contributed to the remarkable dipole moment (0.3354 \(\times\) 10\(^{-29}\) C m).

Ferroelectricity, one of the most important properties in materials, is inseparable from the asymmetry, and is usually concomitant with second-order NLO [201, 202]. Notably, the highly free motions of organic cations provide more opportunities to obtain ferroelectricity [203]. Wu et al. alloyed aliphatic amine into classical 3D inorganic perovskite CsPbBr\(_3\) to break the primary crystal symmetry [186]. The resultant (C\(_2\)H\(_5\)NH\(_3\))\(_2\)CsPb\(_2\)Br\(_7\), has striking ferroelectricity (ca. 4.2 \(\mu\)C/cm\(^2\)) and a higher Curie temperature \(T_c\) (412 K) than the prototype of BaTiO\(_3\) \(T_c\) (393 K). From the room temperature to \(T_c\), it exhibited temperature-dependent SHG response (Figure 14A) as the asymmetry elements decreased in another perovskite phase (Figure 14B–E). In fact, SHG measurement has been a sensitive and valid avenue to identify the asymmetry or the special phase conversion between asymmetry and symmetry [204]. Li et al. devised the highly polarization-sensitive 2D hybrid perovskite ferroelectric \((\text{CH}_3\text{CH}_2\text{NH})\text{PbBr}_4\) for detecting shortwave polarized light [187]. The P-E hysteresis loop records demonstrated the superior spontaneous polarization \(P_s\) of 3.6 \(\mu\)C/cm\(^2\) at 318 K, and the detectable SHG response revealed a stable NLO intensity of around 0.4 \(\times\) potassium dihydrogen phosphate (KDP) at room temperature. The self-made detecting device of perovskite ferroelectric also demonstrated a huge dichroism ratio \((I_{\parallel}/I_{\perp} = 2.0)\) coupling with exceptional sensitive detectivity (~10\(^{10}\) Jones) and nimble responding rate (~20 \(\mu\)s) in the shortwave region. Recently, the same group explored the antiferroelectric 2D multilayered hybrid perovskite (BA\(_x\))\(_{1-x}\) (EA)\(_x\)PbI\(_{3-x}\) (BA = n-butylammonium and EA = ethylammonium) at high temperature [188]. Emerging highly temperature-dependent SHG activities confirmed the existence of acentric structure in this perovskite. The P-E hysteresis loops verified the existence of ferroelectricity and antiferroelectricity, accompanied by...
biaxial ferroelectricity with a $P_s$ of 5.6 μC/cm² (room temperature) and a high Curie point (~363 K). Meanwhile, brilliant energy storage efficiencies (65%–83%) conferred it with the potential for efficient electric energy storage. Aside from ferroelectricity, piezoelectricity is also intimately involved in the noncentrosymmetry as well as NLO of the materials [205–207]. However, the majority of the 2D piezoelectrics reported are all-inorganic ones. For instance, CsLaNb2O7 [208], RbBi2Ti2NbO10 [209], CsBi2Ti2TaO10 [209], and LiRtTiO3 [210] (R = rare earths) piezoelectrics all manifest characteristic asymmetry with clear SHG signals.

Table 1: 2D perovskites for NLO.

<table>
<thead>
<tr>
<th>Chemical formula</th>
<th>Metal</th>
<th>Halogen</th>
<th>Organic ligand</th>
<th>Phase</th>
<th>NLO property</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2mepht)PbBr4</td>
<td>Pb</td>
<td>Br</td>
<td>2-Methyl-1,5-diaminopentane</td>
<td>R-P</td>
<td>SHG</td>
<td>[185]</td>
</tr>
<tr>
<td>(C,H4,NH3)2CsPb2Br7</td>
<td>Pb</td>
<td>Br</td>
<td>C,H4,NH3</td>
<td>R-P</td>
<td>SHG</td>
<td>[186]</td>
</tr>
<tr>
<td>[CH3(CH2)2NH3][CH3NH3]Pb2Br7</td>
<td>Pb</td>
<td>Br</td>
<td>CH3(CH2)2NH3, CH3NH3</td>
<td>R-P</td>
<td>SHG</td>
<td>[187]</td>
</tr>
<tr>
<td>(BA)2(EA)Pb1.10</td>
<td>Pb</td>
<td>I</td>
<td>n-Butylammonium, ethylammonium</td>
<td>R-P</td>
<td>SHG</td>
<td>[188]</td>
</tr>
<tr>
<td>[(C,H4,NH3)2PbCl3</td>
<td>Pb</td>
<td>Cl</td>
<td>C,H4,NH3</td>
<td>R-P</td>
<td>SHG</td>
<td>[189]</td>
</tr>
<tr>
<td>R/S-(MPA)1.5PbBr3·0.5(DMSO)</td>
<td>Pb</td>
<td>Br</td>
<td>Methylphenylammine</td>
<td>–</td>
<td>SHG</td>
<td>[148]</td>
</tr>
<tr>
<td>R/S-LIPF2PbI4</td>
<td>Pb</td>
<td>I</td>
<td>R/S-1-(4-chlorophenyl)ethylammonium</td>
<td>R-P</td>
<td>SHG</td>
<td>[190]</td>
</tr>
<tr>
<td>(C,H4,NH3)2,Cb2Br7</td>
<td>Pb</td>
<td>I</td>
<td>C,H4,Cb2, NH3</td>
<td>R-P</td>
<td>THz</td>
<td>[191]</td>
</tr>
<tr>
<td>(C,H4,NH3)2PbBr6</td>
<td>Pb</td>
<td>Br</td>
<td>C,H4,NH3</td>
<td>R-P</td>
<td>THG</td>
<td>[192]</td>
</tr>
<tr>
<td>(C,H4,NH3)2PbI6</td>
<td>Pb</td>
<td>I</td>
<td>C,H4,NH3</td>
<td>R-P</td>
<td>THG</td>
<td>[193]</td>
</tr>
<tr>
<td>(C,H4,NH3)2(CH2)2NH3Pb2J10</td>
<td>Pb</td>
<td>I</td>
<td>C,H4,NH3, CH2NH3</td>
<td>R-P</td>
<td>THG</td>
<td>[193]</td>
</tr>
<tr>
<td>(C,H4,NH3)2(CH2)2NH3Pb2J10</td>
<td>Pb</td>
<td>I</td>
<td>C,H4,NH3, CH2NH3</td>
<td>R-P</td>
<td>THG</td>
<td>[193]</td>
</tr>
<tr>
<td>(PEA)2PbI6</td>
<td>Pb</td>
<td>I</td>
<td>Phenylammine</td>
<td>R-P</td>
<td>THG</td>
<td>[194]</td>
</tr>
<tr>
<td>(BA)2PbI6/(BA)2MAPb2I7</td>
<td>Pb</td>
<td>I</td>
<td>n-C,H4,NH3</td>
<td>R-P</td>
<td>THG</td>
<td>[195]</td>
</tr>
<tr>
<td>(PEA)2(MA)2PbBr16</td>
<td>Pb</td>
<td>Br</td>
<td>Phenylammine, methylammonium</td>
<td>R-P</td>
<td>THG</td>
<td>[196]</td>
</tr>
<tr>
<td>(C,H4,NH3)2PbBr4</td>
<td>Pb</td>
<td>Br</td>
<td>C,H4,NH3</td>
<td>R-P</td>
<td>3PA</td>
<td>[197]</td>
</tr>
<tr>
<td>(OA)2PbBr4</td>
<td>Pb</td>
<td>Br</td>
<td>Octyl ammonium</td>
<td>R-P</td>
<td>5PA</td>
<td>[198]</td>
</tr>
<tr>
<td>(C,H4,NH3)2PbI4</td>
<td>Pb</td>
<td>I</td>
<td>C,H4,Cb2, NH3</td>
<td>R-P</td>
<td>SA</td>
<td>[199]</td>
</tr>
<tr>
<td>(C,H4,NH3)2(CH2)2NH3Pb2I7</td>
<td>Pb</td>
<td>Br</td>
<td>C,H4,Cb2, NH3</td>
<td>R-P</td>
<td>SA</td>
<td>[200]</td>
</tr>
</tbody>
</table>

Figure 14: Temperature-dependent SHG responses and crystal structures of 2D ferroelectric perovskite. (A) Temperature-dependent SHG signals of (C,H4,NH3)2CsPb2Br7. Inset: the SHG intensity as a function of wavelength at different temperatures. Crystal structures of (C,H4,NH3)2CsPb2Br7 at different temperatures. At 293 K: (B) viewed along the crystallographic b-axis and (C) the perovskite framework. The arrows indicate the relative displacements along the crystallographic c-axis. At 420 K: (D) highly symmetric structure packing and (E) perovskite framework. Reprinted from Ref. [186] with permission from the Wiley-VCH.
diverse cation species. Therefore, it is more usual that the changes of SHG response arise from the change of polarization. Recently, Wei et al. observed the van der Waals (vdW) interplay in 2D hybrid perovskite \((\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbCl}_4\) nanosheets with a polar space group \((\text{Cmc}2_1)\) distribution via SHG measurements [189]. The polarized SHG along the crystallographic \(b\)- and \(c\)-axes and the anisotropy of SHG intensity as displayed in Figure 15A and B implied the decayed signal intensity owing to the minute variety of vdW interactions as thickness of nanosheets decreased.

As mentioned, the incorporation of chiral functional groups can induce the NCS space groups of 2D perovskites, facilitating the formation and application of second-order NLO effects. For example, the 2D chiral perovskite nanowires \(R\)-(MPEA)\(_{1.5}\)PbBr\(_{3.5}\)(DMSO)\(_{0.5}\) elucidated in section 3.1 manifested prominent SHG signals pumped under lasers at diversified wavelengths (Figure 16A). It exhibited a high second-order NLO coefficient \((d_{eff})\) \(\sim 0.68\) pm/V with a laser damage threshold of \(8.6 \times 10^4\) W/cm\(^2\). Detailed polarization-dependent SHG measurements verified that the chiral perovskite also displayed a remarkably large polarization ratio up to 96.4\% under linearly polarized laser (Figure 16B), and also clear nonlinear optical CD under circularly polarized pump light (Figure 16C). Shortly afterward, Yang et al. incorporated homochiral cations \((R/S\)-LIPF, LIPF = 1-(4-chlorophenyl)ethylammonium) to the 2D lead iodide perovskite along with ferroelectric and SHG reactions [190]. This pair of synthesized enantiomers by convenient molecular modulations crystalized in the polar \(P1\) space group at room temperature, suggesting the presence of spontaneous polarization (a calculated value

![Figure 15: Thickness-dependent SHG responses of 2D perovskite.](image)

(A) Polar SHG intensity plots of the 2D \([\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbCl}_4\] perovskite nanosheets. The dots represent the experimental data, and the solid curves indicate the theoretical fits. (B) SHG intensity anisotropy \((I_{c-axis}/I_{b-axis})\) dependent on the thickness of the measured nanosheets. Reprinted from Ref. [189] with permission from the American Chemical Society.

![Figure 16: NLO characteristics of the chiral \((R\)-(MPEA)\(_{1.5}\)PbBr\(_{3.5}\)(DMSO)\(_{0.5}\) perovskite.](image)

(A) Normalized NLO spectra of a \((R\)-(MPEA)\(_{1.5}\)PbBr\(_{3.5}\)(DMSO)\(_{0.5}\) nanowire pumped at various wavelengths. (B) SHG intensity from a horizontally oriented \((R\)-(MPEA)\(_{1.5}\)PbBr\(_{3.5}\)(DMSO)\(_{0.5}\) nanowire as a function of the linear polarization angle as tuned by the \(\lambda/2\) plate. The dots are the experimental data, while the solid lines are the cos\(^4\) \(\theta\) fits. (C) SHG intensity from the nanowire as a function of the rotation angle of the \(\lambda/4\) plate. The pump was left-handed circularly polarized when the rotation angle was 45\(^\circ\) and 225\(^\circ\), and was right-handed circularly polarized when the rotation angle was 135\(^\circ\) and 315\(^\circ\), as indicated by the arrows. Excitation and detection wavelengths are 850 and 425 nm, respectively. The error bars represent the variations between the measurements on the different samples, or the different sites on the same sample. Reprinted from Ref. [148] with permission from the American Chemical Society.
of about 13.96 μC/cm²). The phase transition temperature $T_r$ of R-LIPF ($T_{r(0)} = 483.0$ K) and S-LIPF ($T_{r(0)} = 473.2$ K) perovskite is obviously distinct, varying from the general cases of enantiomers. From the SHG spectra, R/S-LIPF displayed moderate SHG intensity (approximately the half of KDP reference), and the intensity decayed gradually when the rising temperature approached $T_r$, confirming their chiral nature. Hysteresis loop characterizations from piezoresponse force microscopy (PFM) provided a considerable local coercive voltage response ($=112$ V) for the R-LIPF thin film, which clarified the compelling ferroelectric performance and switchable polarization.

Terahertz (THz) radiation, generated from the second-order NLO materials and the frequency concentrated in the range of 0.1 to 10 THz [211, 212], had rapidly developed for communication, detection, and sensing applications. However, the generation and modulation of THz radiation via 2D perovskites are rare. In 2017, Chanana et al. accomplished the selective modulation of THz radiation by a 2D hybrid perovskite (C$_{4}$H$_{9}$NH$_{3}$)$_{2}$PbI$_{4}$ (PEPI) deposited on semiconductor substrates [191]. The bandgaps and exciton absorption band of the multilayered perovskite could be flexibly adjusted through the alternation of layer numbers. Evidently improved broadband THz absorption was observed on the perovskite/silicon wafers in comparison with the pure silicon semiconductor, and the modulation resulted from the transfer of excitation at the interface of perovskite/silicon substrate [213].

### 3.2.2 2D perovskites for third- and high-order NLO

Third-order NLO is foremost in the realm of high-order ($n \geq 3$) NLO, and is not restricted in the NCS configuration. Therefore, a wider diversity of 2D materials can be adaptable in third-order NLO [214, 215]. Saouma et al. explored the third-order optical nonlinearity of a 2D R-P perovskite (CH$_{3}$CH$_{2}$NH$_{2}$)$_{2}$PbI$_{3-n}$ (n = 1–4) via THG [192]. It outperformed its 3D counterpart MAPbBr$_{3}$ and the reference material AgGaSe$_{2}$ in respect of the THG coefficient throughout the IR, with the calculated $\chi^{(3)}$ ranging from $(2.6 \pm 0.5) \times 10^{-11}$ esu to $(5.6 \pm 1.0) \times 10^{-11}$ esu. The laser-induced damage threshold was also improved following the dimensional reduction of perovskites, and these 2D perovskites all possessed high resilience to optical damage. The individual quantum-well structure in 2D R-P perovskites is believed to be beneficial for strengthening the third-order nonlinearity [216].

Abdelwahab et al. mechanically stripped nanoflakes from single crystals of four 2D R-P perovskites, (C$_{4}$H$_{9}$NH$_{3}$)$_{2}$PbI$_{4}$ (Br$_{n}$), (C$_{4}$H$_{9}$NH$_{3}$)$_{2}$PbI$_{3}$ ($n_{x}$), (C$_{4}$H$_{9}$NH$_{3}$)$_{2}$CH$_{3}$NH$_{3}$PbI$_{7}$ ($n_{x}$), and (C$_{4}$H$_{9}$NH$_{3}$)$_{2}$CH$_{3}$NH$_{3}$PbI$_{10}$ ($n_{x}$), separately [193]. These 2D R-P perovskite nanosheets yielded strong THG signals in almost the entire visible scope. The thickness and excitation wavelength had a great impact on THG response. The best THG conversion capability of (C$_{4}$H$_{9}$NH$_{3}$)$_{2}$CH$_{3}$NH$_{3}$PbI$_{7}$ R-Ps is 0.006%/with the third-order susceptibility $\chi^{(3)}$ of $1.12 \times 10^{-17}$ m² V⁻², considerably higher than the conventional 2D materials [217].

Two-photon absorption (2PA) is also an important third-order NLO effect, characterized by a quadratic dependence on the intensity and profound depth [218], which is promising to elevate the light harvesting of solar cells [215] and sensibility of photodetector [219]. Zhang et al. reported the ferroelectric hybrid perovskite (C$_{4}$H$_{9}$NH$_{3}$)$_{2}$CH$_{3}$NH$_{3}$PbBr$_{3}$, single crystals with prominent 2PA [220]. Distinctive bilayered stacking constrained carriers in [Pb$_{2}$Br$_{7}$] octahedral firmly, and thence, a more giant 2PA coefficient of $5.76 \times 10^{-17}$ cm GW⁻¹ was determined than traditional all-inorganic perovskite by the Z-scan technique. Differential scanning calorimetry (DSC) curve unveiled a reversible (322 K/318 K) ferroelectric phase transition, and afforded a spontaneous polarization of 3.8 μC/cm². For the purpose of reinforcing photoluminescence from 2PA, Liu et al. designed a composite construction consisted of SiO$_{2}$ microspheres, which was transferred to uniform 2D perovskite flakes [194]. These 2D perovskite flakes were mechanically exfoliated from the fabricated (PEA)$_{2}$PbI$_{4}$ perovskite films by using a scotch tape, and then the homodisperse dielectric microspheres to cover the perovskite flakes. The hybrid dielectric construction in 2D perovskite flakes not only concentrated the pump laser but also suppressed the nonradiative losses. Under the synergistic effect of microspheres, 2PA-induced

![Figure 17](image-url)

**Figure 17:** Enhanced 2PA-induced emission from a 2D perovskite-microsphere structure. (A) 2PL images of the perovskite flake without (top panel) and with (bottom panel) SiO$_{2}$ microsphere under an excitation power of 0.1 mW, respectively. (B) 2PL spectra for a bare perovskite flake (w/o MS, green curve) and a perovskite-microsphere hybrid dielectric structure (w/t MS, red curve). The SiO$_{2}$ microsphere shows no emission within this waveband (black curve). Reprinted from Ref. [194] with permission from the Wiley-VCH.
photoluminescence emission was improved by two orders of magnitude than the initial perovskite flakes (Figure 17). Apart from the homogeneous perovskite crystals, heterostructures in 2D perovskites are expected to possess distinguished NLO properties. Wang et al. explored the NLO behaviors of (BA)\(_2\)PbI\(_4\)/(BA)\(_2\)MAPb\(_4\)I\(_8\) (BA = n-C\(_4\)H\(_9\)NH\(_3\)) heterostructures [195]. In inhomogeneous heterostructure crystals, the Z-scan pathway was inapplicable to quantify the third-order nonlinear susceptibility, and therefore nonlinear transmittance measurements were performed instead. Combining multiphoton-induced photoluminescence (MPL) from 800 to 1200 nm with nonlinear transmittance measurements, 2D perovskite heterostructures provided a larger 2PA coefficient (44 cm MW\(^{-1}\)) than pure (BA)\(_2\)PbI\(_4\) (4.56 cm MW\(^{-1}\)) and (BA)\(_2\)MAPb\(_4\)I\(_8\) (6.25 cm MW\(^{-1}\)). Additionally, the heterostructures were invested with a high responsivity of 10\(^{−7}\) A W\(^{-1}\) in the IR wavebands. The advanced nonlinear properties might be ascribed to the nonradiative energy transfer by an antenna-like effect in the perovskite heterostructures. Apart from 2PA, the two-photon luminescence (2PL) is also a valuable NLO effect for practical applications such as the biological imaging [221]. Zhu et al. reported a quasi-2D perovskite (PEA)\(_2\)(MA)\(_{n}\)Pb\(_{4}\)I\(_{8\ n}\) (n = 5) via the artful antisolvent processing method [196]. Under the continuous-wave (CW) excitation at 980 nm, the two-photon up-conversion luminescence could be observed resulting from optical exciting the gap states directly. However, the 2PL response became inappreciable while the n was less than 5.

Higher-order NLO effects such as the three-photon absorption (3PA) [222], four-photon absorption (4PA) [223], and even five-photon absorption (5PA) [224] have been carried out to enhance the action of multiphoton absorption (MPA) cross-sections (\(\eta\times\alpha_n\), \(\eta\) and \(\alpha_n\) represent the PLQY and the cross-section, respectively) [225, 226]. The longer penetration depth, minimized background fluorescence, and reduced biological damage from higher-order nonlinear absorptions are desirable for applications in high-resolution imaging, optical limiting, pumped lasing, etc. [227–229]. Recently, Lu et al. compared the difference of 3PA coefficients between multilayered perovskite (C\(_4\)H\(_9\)NH\(_3\))PbBr\(_3\) and its 3D counterpart [197]. On the basis of 2D excitonic quantum perturbation model, the 3PA coefficient was predicted to be 2–7 cm\(^{-1}\) GW\(^{-2}\) at the laser excitation of around 1000 nm. From three-photon-excited photoluminescence (3PL), it is accorded well with the theory speculation, which confirmed the pivotal role of 2D excitons in the enhancement of 3PA coefficient. Moreover, this theory also deduced that low temperature would boost the 3PA coefficient by at least two orders of magnitude due to the low linewidth (<1 meV) of the final excitonic state. Among the traditional semiconductor materials or organic crystals, high action cross-sections of 4PA or 5PA are usually difficult to reach. Chen et al. proposed a self-made core-shell halide perovskite colloidal nanocrystal involving 3D MAPbBr\(_3\) core and (OA)\(_3\)PbBr\(_4\) shell (OA = octyl ammonium) with ultrahigh 5PA coefficient [198]. The wrapped (OA)\(_3\)PbBr\(_4\) shell around the core supplied stronger quantum confinement for MAPbBr\(_3\), and effect surface passivation, corresponding to the boosted value of \(\alpha_n\) and PLQY in contrast to the bare MAPbBr\(_3\) nanocrystals [230–232]. From the Z-scan measurements at 800 nm wavelength, core-shell multidimensional perovskite indicated a giant \(\eta\alpha_n\) of approximately \(10^{-13}\) cm\(^{10}\) s\(^4\) photon\(^{-1}\), which are nine orders of magnitude higher than the reported organic dyes [233].

The astonishing optical nonlinearity and higher stability of 2D perovskites had expanded their applications to ultrafast laser optics. Laser emission originating from saturable absorption (SA), an acknowledged NLO behavior, could filter out low-intensity light selectively [234]. Differing from the previous reports about pulse generation from 3D perovskite nanosheets [235], Hong et al. prepared a thin film of 2D hybrid perovskite (C\(_4\)H\(_9\)C\(_2\)H\(_4\)NH\(_3\))PbI\(_3\) (abbreviated as PEPI) crystallites for ultrafast mode-locking of fiber laser [199]. Based on the PEPI functioning as a saturable absorber, short transform-limited soliton pulses (381 fs) covered C- and L-bands in the anomalous regime. In the normal dispersion regime, the dissipative soliton pulses were formed at the center of 1561.2 nm with a stable pulse duration of 3.4 ps and attendant great repetition. Besides, the wavelength of laser could be tuned facilely in C- and L-bands via altering the optical gain. Fu et al. designed large-area microring laser arrays from 2D R-P perovskite (BA)\(_2\)(MA)\(_{n}\)Pb\(_{4}\)Br\(_{8\ n}\) through the PDMS (polydimethylsiloxane) template pathway in confined solution [200]. In the process of amplified spontaneous emission (ASE), it was found that the n = 6 fabricated microrings illustrated a superior gain coefficient (G) of 112 cm\(^{-1}\) from the variable stripe length (VSL) method and a low threshold fluence of 13.6 \(\mu\)J cm\(^{-2}\), which depicted much better performance than the previously reported 3D perovskite analogs [236, 237]. In the whispering-gallery-mode, the uniform thin-film acquired a high cavity quality factor of \(\approx\)2600.

4 Conclusion and outlook

In this view, we highlight the major advances and developments of 2D organic-inorganic hybrid perovskites for optical applications, with a particular focus on the NLO.
As a sort of high performance semiconductor materials, the low-cost and simple fabrication processes have obtained unprecedented appreciation than these conventional 2D semiconductor materials such as graphene, TMDs, and BP which demand large capital investment and tedious work. Meanwhile, the species of organic cations are more abundant than inorganic cations, and the variety of these organic cations render 2D hybrid perovskites high freedom and flexibility in adjusting the interlayer distance and distortion of structures. The special and naturally formed multiple quantum wells effect arouses huge exciton binding energy and higher stability, and the significant parameter layer numbers \( n \) also play a crucial role in regulating the bandgap of perovskites, making them a hot shot for applications in photonics and optoelectronics. Not only that, the introduction of chiral organic functional groups breaks through spatial symmetry in traditional hybrid perovskites, therefore, it expands an innovative avenue for second-order NLO in 2D perovskites by handy modifications. Nevertheless, the researches and technologies of this field are still in its infancy. For instance, the studies of generation, detection, and modulation of THz, sum-frequency generation (SFG), difference-frequency generation (DFG), and Pockel effect are still worth further exploring. In third-order and higher-order NLO, 2D hybrid perovskites serve more plentiful functions in optics and optoelectronics: solid state emission, nanolasers, solar cell, photodetector, LED, etc. It is also worth mentioning that the plasmonic nanostructures own exceptional capabilities of boosting the light-matter interaction in 2D hybrid perovskites by plasmonic excitations [238]. By incorporating plasmonic metallic nanoparticles, the performances of optical and optoelectronic materials in perovskites-plasmonic semiconductors will be advanced remarkably [239, 240]. The enhanced nonlinearity from plasmonic effects have developed the new domain of nonlinear plasmonics. Elevated SHG, THG, multi-photon absorption, or emission, etc. have been observed in 2D perovskites with facile plasmonic nanoparticles. In addition, the plasmonic effect shows the enormous potentials in creating the lower-power, lower-size, and rapid responsive optical devices [241].

However, there also exist some downsides which are not negligible, including the instability under heat, light as well as moisture, and the toxicity issues derived from heavy metals. Though the insertion of organic cations strength the resistance and adaptability of 2D perovskites, it cannot tackle these problems essentially. Unlike other 2D materials [242–244], the high content of heavy metal and halide elements also hinder their applications in the biomedical sector, even though their NLO properties are suitable for bioimaging and biosensing. In order to abate and even eliminate toxicity in Pb-based perovskites, some researches concerning lead-free hybrid perovskites had sprung up. However, the implementations of 2D lead-free hybrid perovskites in NLO are rare and still in their infancy. Hence, instability and toxicity in 2D perovskites are the primary factors to hamper the developments in academia and industry. Moreover, the advent of the 2D perovskite heterostructures also offers a fresh approach to the improved performances. The integrations of BP, TMDs, graphene, etc. could form the tunable barrier for charge carrier transport and photogating effect to optimize the performance, such as sensitiveness of photodetectors or phototransistors, of original perovskite materials and trigger their nanophotonic functionalities. In this regard, high-quality, long-term stable, environment-friendly, and more efficient 2D organic-inorganic hybrid perovskites will pave the way for more inclusive applications in photonics, electro-optics, photoelectric, and other important cross-disciplinary domains.

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