Design and Development of Hybrid Halide Perovskites in Laser Devices

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Abstract: Organic-inorganic hybrid halide perovskite is a significant semiconductor material in photonics. Their outstanding optoelectronic characteristics have been reported, increasing energy conversion efficiency of perovskite solar battery by up to 25.5%, which is expected to be major competitors in silicon industry. According to the fundamentals of physics, a viable candidate for a light emitter must really be a superior direct band gap material. Even though there are a lot of papers on perovskite-based light emitting devices in this area, the corresponding laser devices are still lack of research. Here, since the first publication of lasing in hybrid perovskites in the 1990s, great effort has been made especially in 2014. Halide perovskites have the potential to revolutionize the nanophotonics field due to their solution-processed gain medium, almost defect-free semiconductor formation, high luminous efficiency, flexibility of nanostructure, excellent stability, and wide wavelength tunability. This article highlights the important researches on the optical gain from diverse hybrid halide perovskite material and the future challenges of lasing.

Keywords: Hybrid Halide Perovskites, Photonics, Laser Devices, Gain Medium.

1. Introduction

$CaTiO_3$ was first discovered by Gustav Rose in 1830s. It is named "Perovskite" in tribute to mineralogist L.A. Perovski. Following that, the corner-sharing metal halide octahedra that make up the halide perovskite material, also known as crystal structure ABX_3 (A: organic or inorganic cations, B: cations, X: halide anions), are arranged in a three-dimensional framework. Due to the flexibility of this composition, which has received much attention, its optical and electrical characteristics can be properly modified to fulfill the requirements for applications including solar battery [1], photodetectors [2], light-emitting devices [3], scintillators [4], lasers, etc.

In the 1960s, the advent of the semiconductor solid-state laser caused a technological revolution, and laser applications are now widely used in military, factory, medical and scientific research fields. The top contenders for solution-treated luminescence and laser devices in the 1990s were organic semiconductors [5]. For lasing, organic semiconductors are advantageous to have high spectral absorption factor, direct energy band gap, low-cost solution processability, long carrier lifespan, and a high external luminescence efficiency. Hybrid halide perovskite material is one of the most promsing semiconductor in photoelectric field. What is more, it is practical to control the composition of the band gap of perovskite semiconductors, allowing the entire spectrum to be covered when these materials are used in light emitting devices. Moreover, the hybrid or inorganic perovskite materials' low-cost solution processability and optimsed electron-hole transport, as opposed to convective preparation techniques like chemical vapor deposition, enables sustainable mass manufacturing and application to flexible wearable optoelectronics products. Lasers based on hybrid halide perovskite are the one of the newest perovskite optoelectronic devices, which are expected to create low-cost and efficient laser diodes. Lasing generated by $MAPbX_3$ films and amplified spontaneous emission (ASE) and at room temperature (RT) were accomplished in 2014, launching a new light-emission direction [6]. These merits make hybrid halid perovskite have the potential to be a gain medium for lasing, which provide perovskite laser-based optoelectronic applications a strong boost.

The progress achieved in lasing field is covered in the following sections, along with an overview of the significant research project that has been underway since 2014 on the use of hybrid halide perovskite materials as gain medium in laser devices and a discussion of their gain mechanisms and challenges ahead.

2. Literature Review Section

2.1 ASE/Lasing from Hybrid Perovskites

The first optically pumped lasing using solution-processed 3D hybrid perovskites has been accomplished ($MAPbX_3$, 65 nm thin films). The ASE threshold has been reported to be 12 ± 2 μJ/cm^2 with a high carrier density, competing with the most advanced solution-processed gain medium. Due to its characteristics of high optical absorption coefficients, tiny capture cross sections, and delayed Auger recombination, the ASE threshold is quite low [6]. More significantly, $MAPbI_3$ is a very durable gain medium capable of producing constant ASE intensity and its mean intensity is only 0.2 % standard deviation at 26 h continuous irradiation (1 kHz Ti sapphire regenerative amplifier). This superior photostability demonstrates the potency and high performance of solution-processed hybrid halide perovskite as a gain medium. By directly combining different prophase resources, it is simple to change the formation of perovskite films to realize broad wavelength tunability covering visible band (Figure 1a). A $MAPbI_3$ perovskite film may also have its threshold fluence for ASE decreased by at least two orders of magnitude by being sandwiched in a cavity made up of a thin film reflector and a gold-backed reflector (Figure 1b) [7]. A vertical cavity laser based on a $MAPbI_{3-x}Cl_x$ layer was used by Deschler et al. [8] (Figure 1c, d). Besides, the planar structural approach of 2D perovskite films may also be used to control perovskite laser. In 2015, Saliba et al. [9] constructed a surface emitting distributed feedback (DFB) cavity perovskite laser, which is a key solution in realizing an extremely low threshold all-electric pumped injection laser (0.32−2.11 μJ/cm^2). By simply altering the grating periodicity, the lasing may be modulated between 770 and 793 nm (Figure 1e, f).These perovskite films have great promise for easily manufacturing low-cost, widely tunable, stable and single-mode lasers. Therefore, hybrid halide perovskite materials exhibit extremely high performance characteristics and are a latest kind of low-cost solution-treated optical-gain medium.

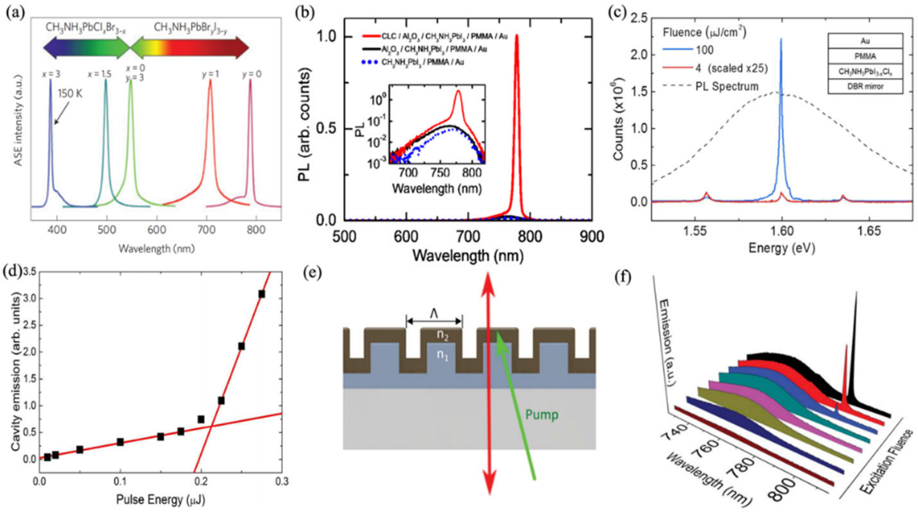

Figure 1. (a) Tunable ASE in hybrid 3D halide perovskite films [6]. (b) emission from the stack with pulsed excitation [7]. (c) $MAPbI_{3-x}Clx$ emission spectra at various pump fluences. (d) The PL intensity of vertical cavity laser [8]. (e) Illustration of DFB cavity patterned perovskite structure. (f) PL spectra from a DFB laser based on perovskite film [9].

Table 1 below provides a summary of current significant results and important ASE/lasing characteristics from hybrid perovskite gain medium. These hybrid halide perovskite films with different nanostructures and cavities lasers have different laser thresholds and functional characteristics.

Table.1. Typical ASE/lasing results from different hybrid halide perovskite materials

Material ($X = Cl^-$, Br^-, I^-)	Nanostructure Type	Pumping Source	Emission Wavelength [nm]	Laser Threshold (ASE or Lasing) [μJ/cm2]	Cavity	Reference
$CH_3NH_3PbX_3$	Thin film	150 fs @ 600 nm	≈500–790	≈12 (ASE)	N.A.	Xing [6].
$CH_3NH_3PbI_3$	Thin film	4 ns @ 530 nm	≈780	≈10 (ASE)	N.A.	Stranks [7].
$CH_3NH_3PbI_{3-x}Cl_x$	Thin film	400 ps @ 532 nm	≈760	≈120 (ASE) ≈0.2 μJ (lasing)	N.A. Vertical microcavity	Deschler [8].
$CH_3NH_3PbI_3$	Thin film	2 ns @ 355 nm	≈775	≈65 (ASE) ≈75 (lasing)	N.A. Spherical WGM	Sutherland [10].
$CH_3NH_3PbBr_3$	Square microdisk	120 fs @ 400 nm	≈550	≈4 (lasing)	Planar WGM	Liao [11].
$CH_3NH_3PbI_{3-x}X_x$	Microplatelet	50 fs @ 400 nm	≈760	≈40 (lasing)	Planar WGM	Zhang [12].
$CH_3NH_3PbI_3$	Microcrystal networks	0.8 ns @ 355 nm	≈ 765	≈200 (lasing)	Random lasing	Dhanker [13].
$CH_3NH_3PbX_3$	Nanowires	150 fs @ 402 nm	≈500–780	≈0.2 (lasing)	Fabry-Perot cavity	Zhu [14].

From the comparison different hybrid halide perovskite materials as gain medium, excellent lasers require high quality optical feedback achieved through well-defined resonators cavity, and the next section will focus on three representative cavities: Fabry-Perot cavity, Whispering Gallery Mode cavity and Random Lasing.

2.2 Fabry-Perot Laser Cavity Architecture

Perovskite micro/nano lasers have advanced quickly due to composition, structure, and morphology engineering. Since the large refractive indices difference caused by gain medium and air, this interface be viewed as a high reflectance mirror of the microcavity. The simplest cavity is the Fabry-Perot (FP) Laser Cavity, which is made up of not less than two reflecting surfaces between which the active medium (pervoskite) is placed. FP cavity based perovskite lasers provide wider range selectivity in laser spectrum and power output.

In 2015, the first nanowires made of a single crystal of lead hybrid halide perovskite ($MAPbX_3$) for lasing was researched by Zhu et al. [14]. Single crystal optical traps that have been low temperature solution processed and have great optical quality, adequate size and stable carrier transport are excellent candidates for FP lasers. The perovskite NW laser performed superbly (Figure 2a, b), exhibiting 400 nm optical pumping, low laser threshold (0.22 μJ/cm^2), and broad wavelength tunability band (500-790 nm). Fu et al. [15] took a step in the right direction by enhancing the thermal and optical stability of hybrid perovskites. In 2016, it was reported that $FAPbX_3$ Naonwires with lengths ranging (6-30 μm) have grown in low-temperature solutions, which were shown to exhibit low lasing thresholds (6 μJ/cm^2) and high Q-Factor under pulsed laser stimulation. The NW lasers showed the broad tunable wavelength (490-820 nm), and compensated the gap in laser wavelength that could not be reached previously with MA-based perovskites through substituting cations and anion (Figure 2c, d).

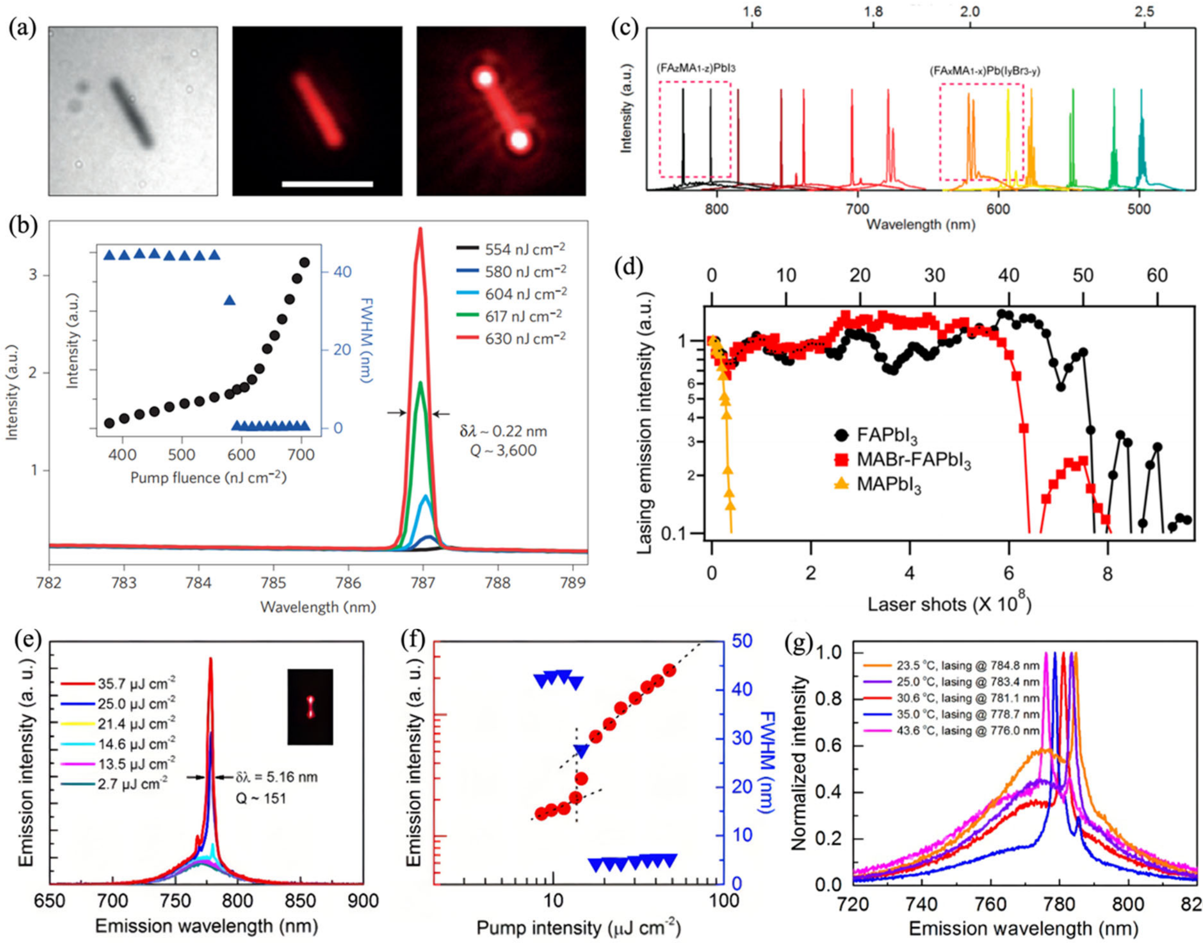

Figure 2. (a) Optical characterization (left) of single NW. NW emission near lasing threshold (middle and right). (b) Emission spectra of NW at the lasing threshold. (Inset: pump intensity) [14]. (c) Wavelength tunability of perovskite NWs lasing. (d) Emission stability of different lead perovskite NW lasing [15]. (e) Spectra of emission for various pump intensities (Inset: a lasing plasmonic NW). (f) The relationship between integrated emission intensity and FWHM. (g) Temperature-dependent lasing behavior's normalized spectra [16].

In addition, Yu et al. [16] suggested a different kind of heat-resistant perovskite ($CH_3NH_3PbI_3$) NWs. The single crystal hybrid perovskite NWs that had been produced were used as an active medium placed in plasmonic-based lasers. In contrast to FP nanowire-based devices, the latter laser design is particularly appealing and can produce light below the diffraction limit to subwavelength limits. Under optically pumped, the threshold range (13.5-56.3 $\mu J/cm^2$) depending on the length of the $MAPbX_3$ nanowires at RT, and lasing operate well even at temperatures up to 43.6 °C (Figure 2e, f, g).

2.3 Whispering Gallery Mode Cavity Architecture

In the WGM cavity, the light propagates around a concave surface to amplify traveling wave, in contrast to the FP cavity. Additionally, the principle of WGM cavity is based on total internal reflection (TIR) because of the significant disparity in refractive indices at the interface between the gain medium and air. Material absorption from the gallery's construction within the cavity causes higher losses and less severe optical confinement that oscillating radiation encounters are the causes of the higher threshold values. These lasers might be used in quantum information field.

In 2014, hybrid organic-inorganic perovskite $MAPbI_{3-a}X_a$ nanoplatelets was first reported by Zhang et al. using a two-step vapor deposition preparation way [12]. WGM cavities can naturally occur in the hexagonal or triangular forms (Figure 3a,b), When they were optically pumped, typical $MAPbI_3$ ($MAPbI_{3-a}X_a$) nanoplatelets displayed a threshold range (37-128 $\mu J/cm^2$), a quality factor

(650-900) with near-infrared lasing. In contrast, one-step self-assembly was used by Liao et al. to create a square microdisk laser based on $MAPbBr_3$ perovskite [11]. Excited by a pulsed laser, with a quality factor (430) and a threshold (3.6 μJ/cm^2), single-mode lasing (557.5 nm) was accomplished in a square MD (Figure 3c, d, e). The WGM laser can also be observed in cross sections of $MAPbBr_3$ microrods [17], and the shortest lasing FWHM (~1 nm) at the threshold with pulsed stimulation. (Figure 3f, g).

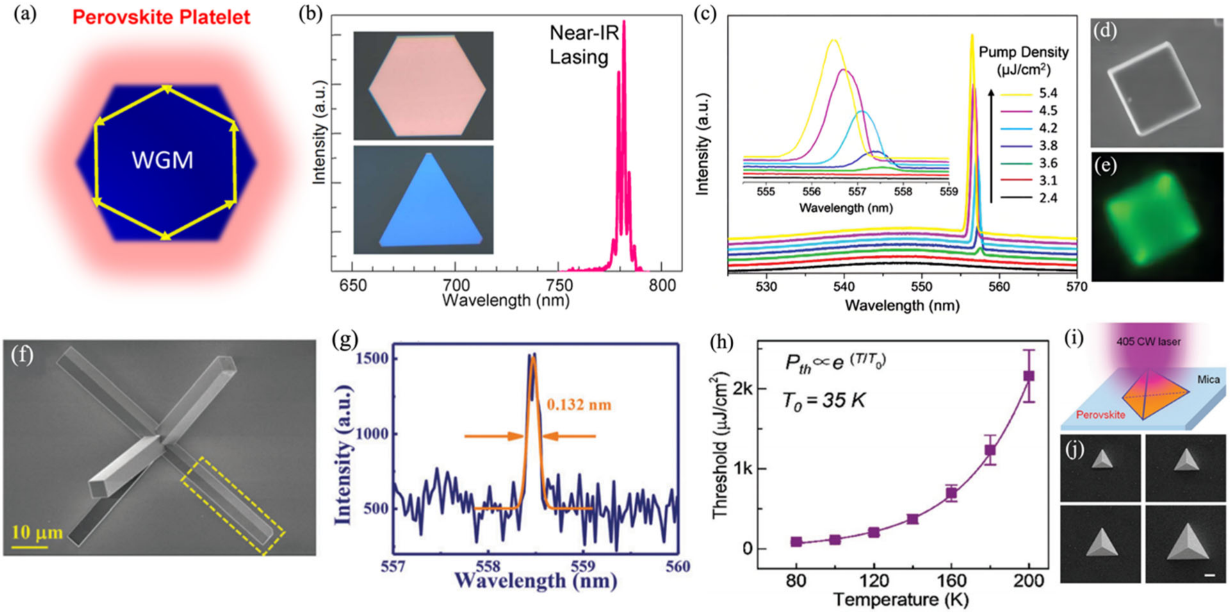

Figure 3. (a) NP laser with a hexagonal structure. (b) The NP 's lasing spectrum; insets: NPs' optical pictures [12]. (c) The square MD's pump-intensity emission spectrum. With a clear blue shift, the locally enhanced spectra are shown in the inset. (d) The square MD. (e) The optical representations of an MD at various pump intensities [11]. (f) SEM picture of the $MAPbBr_3$ microrod. The optical pumping region is located beneath the rectangular box with a yellow dash. (g) The fitted threshold FWHM and laser spectrum [17]. (h) The $MAPbBr_3$ pyramid's cube-temperature-dependent corner's lasing threshold (80-200 K). (i) Illustration of $MAPbBr_3$ pyramid on mica substrate. (j) SEM pictures of $MAPbBr_3$ pyramids with edges (4-8 μm) [18].

Besides, perovskite semiconductors are promising materials for implementing nanophotonic devices mainly because of their alluring physical characteristics, particularly their energy bandgap and strong optical gain. The cube-corner pyramid form of the high-quality $MAPbBr_3$ single crystals Mi et al. [18] supplied is unusual in that it was created on mica substrates using the CVD method. The three facets serve as highly effective reflectors. Under optically pumped by femtosecond laser pulses, lasing was detected from 80 to 200 K between the 92 μJ/cm^2 and 2.2 mJ/cm^2 threshold range (Figure 3h, i, j). These perovskite WGM lasers with outstanding performance are excellent candidates as precursors for ultra-compact, good repeatability, low threshold and high tuning efficiency.

2.4 Random Lasing Architecture

Random lasers, in contrast to conventional lasers, do not need extra resonators, assuring inexpensive manufacturing costs and straightforward technical requirements, but they also have some limitations in the output direction and the output spectrum tuning. The random scattering that occurs between the perovskite material's grains is used in the random laser concept as optical feedback to maintain lasing (Figure 4a) [19]. In addition to being an appealing device for energy-saving lighting applications, RLs are a promising candidate technology for electrically driven lasers, biosensors, and optical interconnection since their low spatial coherence and excellent power conversion efficiency.

A random laser operating under an optical excitation was initially described in the $MAPbI_3$ perovskite microcrystal networks in 2014 by Dhanker et al. [13]. The laser's threshold and FWHM were both less than 200 μJ/cm^2 and 0.5 nm, respectively (Figure 4b, c). Under different power excitation, the distribution of spectral modes was not uniform, and most regions of microcrystals were stimulated. Kao et al. further showed the solution-treated hybrid halide perovskite $MAPbI_3$ films' temperature-dependent random lasing properties in 2014 [20]. Using a coating of solution-treated $MAPbI_3$ placed onto an unpatterned substrate at ambient temperature, Safdar et al. [21] demonstrated low-cost random lasing in two modes (single and dual modes) repectively in 2018. The lasing threshold was 10 μJ/cm^2 under pulsed frequency doubled YAG laser stimulation (Figure 4d).

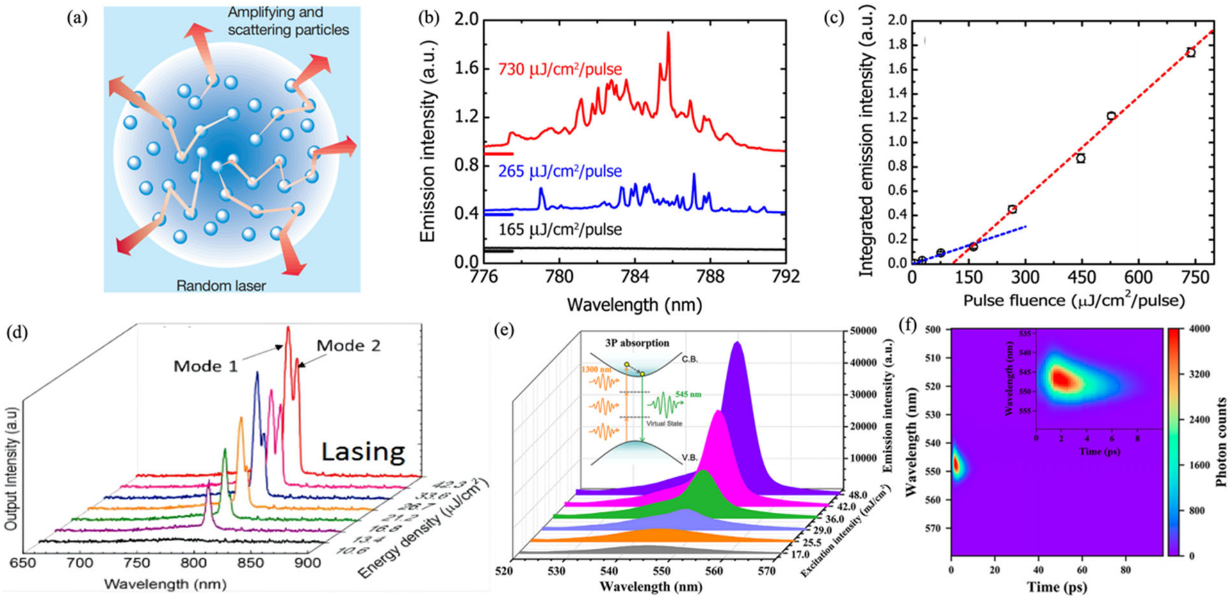

Figure 4. (a) Illustration of the random laser cavity [19]. (b) The different emission spectra of $MAPbI_3$. (c) Excitation pulse fluence and integrated emission intensity [13]. (d) Surface emission spectra for the $MAPbI_3$ film [21]. (e) Emission spectra of 3P excited $MAPbBr_3$ perovskite lasing. Inset: Schematic of 3P emission and absorption. (f) TRPL pictures of RL from the $MAPbBr_3$ film [22].

At present, the technology of random laser based on halide perovskite has limitations in three pluses absorption, only linear single pluse and nonlinear double pluses absorption are available. In 2018, frequency-upconverted RL from halide $MAPbBr_3$ perovskite thin film was achieved through a three-photon (3P) absorption process by Weng et al. [22]. When the stimulation power exceeds the threshold, the time-resolved photoluminescence (TRPL) picture, which displays the ultrafast lasing activity, demonstrates a change with small emission peak and short decay period. (Figure 4e, f). This study is of guiding significance to the application of high order nonlinear optics.

3. Conclusions

Hybrid halide perovskites have the potential to duplicate their ground-breaking properties in photoelectric conversion efficiency and luminous emission. Utilization of diverse gain medium and laser cavity architectures has evolved in the field of hybrid perovskite lasers since 2014, particularly in the context of micro/nanolasers. This article has summarized the design and development of lasing based on hybrid halide perovskites. These are separated into hybrid halide nanostructural perovskite materials, such as NPs, MD, NWs and nanotube for RT ASE/lasing, and representative laser cavity structure: (a) FP Cavities; (b) WGM Cavity; (c) RL architecture. Perovskite is currently employed extensively in a variety of powerful emitters for widespread use, including OELD, optical communication, imaging, etc. Outstanding integration compatibility of perovskite is further guaranteed by their excellent performance and adaptable structure.

High-performance hybrid perovskite micro/nanolasers feature good repeatability, stability, a low threshold, a high Q-factor and high tuning efficiency after optical excitation. The light field may be constrained to a tiny region by the ultra-small volume, which further improves the interaction between light and matter. However, photonic lasers and plasmonic lasers based on hybrid perovskites are limited in size. Since limitations in optical diffraction, microcavities smaller than 1 micron are rarely recorded, especially at wavelength scales. Nevertheless, Optoelectronic integrated systems have a strong chance of realizing subwavelength scale nanolasers due to perovskite's high optical gain, broad absorption segment, and excellent structural architecture.

At present, some challenges of perovskite laser devices remain to be solved. First, environmental operational stability is a prerequisite. The low stability and toxicity (Pb) of perovskite under atmospheric conditions have been researched extensively. Especially for hybrid halide perovskite, the spectral tunability, solution workability, purity and repeatability will be fully exploited under stability conditions to extend the operational life of the corresponding devices. And 2D perovskite semiconductors are also a good solution because they are more environmental stable than 3D, but their photoelectric properties are still inadequate, which is also a challenge that should be overcome. Encapsulation is another useful technique for enhancing device stability, but it might result in bulky, ineffective devices. Besides, the optical-electrical characteristics of perovskite are also essential for upcoming optoelectronic devices. In order to develop effective functional devices, Auger losses and charge transport may be managed by realizing the behavior of electrons and holes. In addition, the device's volume and compatibility might also have an impact on the high-density integrated circuit.

Finally, electrically powered laser device development has more immediumte practical implications. Adoption of transparent conductive electrodes, such as the use of reduced graphene oxide (rGO) and other metal oxide anodes, which could accelerate the produced laser extration, is crucial for the formation of electrically powered laser systems. Future research on this important material will make it easier to be used as an electrically driven laser source, demonstrating the prospect of hybrid halide perovskite for other applications besides solar cells.

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