Advances in small perovskite-based lasers

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Lead Halide Perovskite Nanostructures for Small Lasers

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Abstract:

Lead halide perovskites have recently become rapid growing research field for its great potentials in next generation solar cell and photonic sources. As direct band-gap semiconductors, perovskites are also promising candidates for low threshold and multicolor lasing devices due to its high optical gain, ease of band gap engineering, large absorption coefficient and low defect states. In particular, low dimensional perovskite structures including nanoplatelets, nanowires, quantum dots, are crucial for development of micro or nano-sized laser sources for optical chip and high-resolution imaging, etc. Here we focus on perovskite nanophotonics, in particular lasing properties of perovskite nanostructures. The rapid advance of small lasers based on perovskite nanostructures using both active and passive microcavities will be reviewed, which are mainly classified into four sections: three-dimensional thin film, two-dimensional nanoplatelets, one-dimensional nanowire to zero-dimensional quantum dots. Lasing performance in terms of threshold, color-tunability, spectra-coherence and stability is introduced from both materials and microcavity respects. Fundamental photo-physic mechanisms involved in photoluminescence lasing process, from absorption, emission to gain, are discussed in order to provide insightful understanding lasing properties of different types of perovskites. Finally, a few future prospects on perovskite lasing devices are provided.

1. Introduction

Laser is a coherent light emission device with strong intensity and perfect directionality. It is essentially a light amplification process by stimulated emission of radiation. Over the decades since laser was invented in 1960, lasers have been widely used in a variety of technological and scientific fields, such as bio-imaging, manufacturing, spectroscopy and optical communications.^[1-5] Particularly, with the emergent progress in nanoscience and nanotechnology, solid state small lasers, i.e., the physical size of one or multiple dimensions is comparable or smaller than the diffraction limit, have attracted considerable attention driven by the need of high density data storage, optical integration and high resolution bio-imaging etc.^[6-8] Over the last three decades, a large number of inorganic and organic semiconductor nanostructures with atomic-level flat facets, *i. e.* nanowire (NW) and nanoplatelets (NP) *etc.*, were utilized to function as active optical microcavities for small laser devices. In 2001, Yang and co-authors realized the first optically pumped NW photoluminescence (PL) lasing from single crystalline ZnO NWs.^[8] In 2005, Lieber and co-authors established an electrically driven luminescence lasing from individual CdS nanowires.^[9] To date, lasing have been achieved in a variety of top-down/bottom-up fabricated semiconductor nanostructures, quantum dots (QDs) doped in photonic crystals (PHC), dielectric spheres coated with gain materials and random systems, *etc.*^[10-14] Furthermore, nanolaser device based on amplification of surface plasmon by stimulated emission of radiations (SPASER) pushes the dimension of laser devices into nanometer region.^[15-24] Despite these great success in solid state microlasers and nanolasers, so far small laser devices still extensively suffer from large optical losses and thus high lasing threshold. The carrier density threshold at room temperature of photonic micro-lasers is in the order of $\sim 10^{11} \text{cm}^{-2}$ or higher.^[25, 26] The plasmonic lasing threshold is even 2-3 orders higher than

photonic lasers due to large Ohmic losses of metallic cavities.^[27] Continuous wave operated and electrically injected small lasers, which are essential for practical application in integrated optical chips, are extremely limited so far. For fundamental goals of technological applications, it is urgent to explore new semiconductors with high gain and low losses.

Metal halide perovskites (perovskites) are an interesting group of semiconductor materials with generic chemical formula of AMX_3 or A_2MX_4 , where A is a cation which could be inorganic or organic cation (Cs^+ , $CH_3NH_3^+$, $NH_2CH=NH_2^+$, *etc*), M is divalent metallic cation (Pb^{2+} , Sn^{2+} , Mn^{2+} , Fe^{2+} , *etc*), X is halogen anion (I^- , Br^- , Cl^-).^[28-30] Since 2009, perovskites have gained worldwide attention due to its unprecedented success in photovoltaics.^[31-36] The power conversion of solution-processed $CH_3NH_3PbX_3$ ($MAPbX_3$) perovskite solar cell has increased from 3.8% to 22.1% within a few years.^[37-42] Although there are still some debates, it is widely accepted that the high power conversion efficiency of $MAPbX_3$ are attributed to high absorption coefficient ($\sim 10^4\text{ cm}^{-1}$), balanced and long diffusion length ($\sim 100\text{ nm}$ - $100\text{ }\mu\text{m}$), low defect states density (10^9 - 10^{10} cm^{-3}) and bipolar carrier transport properties.^[31, 33, 34] As direct band-gap semiconductors, perovskites also show wide-band tunable emission color and high quantum yield, holding important potential applications in light sources *etc*.^[40, 43-45] Prior to the rapidly studies in solar cell, perovskites have been studied as light emitting diodes (LED) devices for a long time.^[46-48] In particular, the recent studies on photo-physical properties, structure engineering, device development have led to the rapid progress of coherent and incoherent perovskite photonic sources.^[43, 49-55] For example, a few groups demonstrated perovskite LED with external quantum efficiency of ~ 8 - 12% using solution-processed and thermal evaporator quasi-two dimensional perovskite thin film, *etc*.^[43, 51] Furthermore, low dimensional perovskites structures including NWs, NPs, quantum dots (QDs) are also attracting more and more attention for exploring nanophotonic

and quantum devices including single photon sources, optical detector, transistors, optical sensors, *etc.*^[56-59] In a nutshell, despite the Pb toxicity and poor stability, perovskites have been attracting more and more attention in divergent research areas. These fundamental and application studies on perovskite photonic sources would extensively push forward our present energy and communication technology.

With high absorption coefficient and low defect density, perovskites are excellent gain materials for development of high performance lasing devices. More interestingly, thanks to the long distance ambipolar carrier transport properties, perovskite could greatly raise possibility of realizing electrically driven microlasers and nanolasers. In 2014, Xing *et al.* demonstrated the first amplification of spontaneous emission (ASE) of low temperature solution-processed $\text{CH}_3\text{NH}_3\text{PbX}_3$ perovskite thin film.^[60] Through embedding $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite thin films into distributed Bragg reflector Fabry-Perot (F-P) cavity, Deschler *et al.* demonstrated the room temperature perovskite lasing.^[49] Beyond these thin films, perovskite nanostructures including two-dimensional NPs, one-dimensional NWs and zero-dimensional QDs are good candidates for solid state small lasers.^[61-67] With the advantages of low-cost fabrication method, perovskite microlasers and nanolasers hold crucial potentials for future integrated photonic sources and flexible nanophotonic devices. The performance of optical pumped perovskite microlasers based on the nanostructures is even better than traditional II-VI/III-V semiconductors in the aspect of threshold, color tunability and spectra coherence, *etc.*^[65-69]

This concept article is to summarize and review the rapid progress in perovskite based photonic laser sources. In particular, we discuss optical gain, optical cavity, spontaneous emission (SE), lasing properties of perovskites from fundamental and application views. The

article is organized as follows: In section 1, we will describe band structure, spontaneous emission and gain properties of perovskites. In section 2 we review perovskite small lasers from solution-processed film, vapor-phase/solution processed NWs and NPs, QDs . Section 3 briefly discusses arrays of perovskite small lasers. Section 4 would conclude and give perspectives of future research areas in perovskite lasers.

Section 1: Energy Band Structure and Spontaneous Emission

1.1 Crystalline Structure

Perovskites can be generally classified into two categories by crystalline structures and therefore chemical formula. As shown in **Figure 1a**, in an ideal cubic perovskite lattice, A, M, X locates at eight corners, body centre and six face centres of the unit cell, respectively. M is surrounded by six X atoms to form a $[\text{MX}_6]^{4+}$ octahedral, which then constructs a three-dimensional octahedral network. A sits at the center position of eight octahedra in the network. The radii of A, M, X atoms should satisfy tolerance formula to maintain perovskite crystalline structure. A could be organic cations consisting of several function groups, whose size is mainly dependent on the length of carbon chain. If the carbon chain is short, such as MA^+ , the spacing between $[\text{MX}_6]^{4+}$ octahedral is large enough for placing the organic cation. The perovskite crystalline structure survives, leading to a general chemical formula of AMX_3 (**Figure 1b**). However, when the organic cation has a long carbon chain, *i.e.*, $\text{C}_5\text{H}_6\text{CH}_3\text{NH}_2^+$ (BA^+), the tolerance formula of perovskite structure cannot be satisfied. The $[\text{MX}_6]^{4+}$ octahedral chains separate to provide enough spacing for organic group. In this case, organic cation group sandwiches between two corner-sharing $[\text{MX}_6]^{4+}$ octahedral layers. The perovskites exhibit two-dimensional layered structure with chemical formula of A_2MX_4 (**Figure 1c**). Due to large dielectric contrast between the organic and inorganic $[\text{MX}_6]^{4+}$

octahedral layers, electron and hole are strongly confined into the octahedral layers and bound together via Coulombic force. The strongly bound electron-hole pair suggests binding energy in the two order of meV, which promises strong light-matter interaction and related applications such as low threshold polariton lasing.^[70, 71]

1.2 Electronic Structure and Band Gap Engineering

The band edge electronic states of lead halide perovskite are mainly built by $[\text{PbX}_6]^{4+}$ octahedral. As shown in **Figure 2a-b**, Filippetti *et al.* calculate band structure and projected density of states (PDOS) of MAPbI_3 perovskites by first-principles density functional theory (DFT) methods.^[72] They found that the minimum of conduction band (CBM) is mainly contributed to p -orbitals of Pb atoms (Pb- p). The electronic states at the maximum of valence band (VBM) are predominated derived from s -orbits of Pb atoms (Pb- s) and p -orbits of I (I- p) atoms. The strong coupling between the Pb- s and I- p orbitals results in small effective mass of holes. As halide elements varying from iodides to chlorides, the lattice parameter decreases, which leads to larger wave function overlap between the orbits and therefore increased band gap. Borriello *et al.* also reported similar theoretical works on Sn-based perovskites.^[73] They found that the organic units A only influence the edge band structure via changing the bonding strength and angle between Pb and halogen atoms in $[\text{PbX}_6]^{4+}$ octahedral, which consequently change energy band gap.

The first principle studies of perovskite electronic structures are consistent with experimental observations of perovskite absorption and emission. Wavelength tunability of perovskite emission throughout the whole visible region is readily achieved by controlling the stoichiometry. One way is to substitute halide elements from chlorides to iodides (**Figure 2c**). By using either mixture of chlorides and bromides, or bromides and iodides, the bandgap of

MAPbX₃ can be continuously tunable throughout the whole visible region from 390 nm to 700 nm.^[60] Another way is to substitute the organic elements with other kinds of organic elements or all-inorganic elements like Cs to tune their emission, which serves a good way to further extend the emission region of perovskites into ultraviolet or near infrared region.^[68] The mix of MA⁺ with CH₂=CH₂⁺ (FA⁺) can expand band gap towards 820 nm.^[42] Incorporating all inorganic cesium elements into organic-inorganic lead halide perovskite not only maintains the excellent emission property, but also greatly improves the stability of perovskites. The quantum yield of CsPbX₃ quantum dots without surface passivation was reported as high as ~96% along with wide tunability of band gap in the whole visible regime.^[65] Perovskites of composition MASnX₃ and CsSnX₃ have an emission wavelength around 900 nm while Sn based perovskite is less stable as exposure to air and water compared with Pb-based perovskite.^[74] The wide tunability of perovskite emission would benefit to develop multicolor coherent and incoherent light sources.

1.3 Exciton and Spontaneous Emission

Exciton is a bound state consisting of an electron and a hole, attracted to each other by Coulombic forces. It is one of the most important elementary excitations and plays key roles in optical emission and transport behavior of semiconductors. As an electric neutrally particle, exciton could be hybridized with photons, plasmons and generated new quantum states which are important for quantum information.^[75] The exciton energy is not only determined by intrinsic band gap, but also highly dependent on materials size, defects, doping and environment, which provides considerable opportunity to realize colorful emission source. Exciton binding energy (E_b) is an important characteristic of exciton beyond its resonance energy, which greatly alters exciton recombination dynamics and transport properties.

Excitons could easily dislocate into free carriers when their binding energy is small than thermal fluctuation energy; otherwise electrons and holes are bound together in the form of excitons. Therefore, in solar cell devices with need of free carriers, it requires semiconductors with small binding energy; as a contrast to develop strong emission or quantum devices, semiconductors with large exciton binding energy are more suitable candidates.^[69]

Exciton behaviors of hybrid perovskite system could not be easily explained either by inorganic or organic semiconductors. Considering their importance in solar cell devices, many experimental and theoretical efforts have been made to study exciton binding energy of MAPbX₃ thin films. Experimentally, in most of perovskites, clear exciton absorption peak could be resolved at room temperatures, indicating large exciton binding energy in these materials. However due to the distinct measurement methods, there are still some controversies on real exciton binding energy of MAPbI₃ thin film. The measured value varies from ~ 2 to 80 meV by different group using optical absorption, emission to electrical methods.^[76-79] As a contrast, the measured E_b value shows good agreement between theory and experiment results from different groups in a simpler system such as pure-inorganic CsPbX₃. Exciton binding energy of perovskite increases when halide element varies from chloride to iodides together with decreasing of their energy band gap. For example, exciton binding energy of MAPbCl₃, MAPbBr₃ and MAPbI₃ thin film and single crystals was reported as ~ 50-120 meV^[80-82], 40-100 meV^[83] and 2-80 meV^[28, 66, 83, 84], respectively. CsPbCl₃, CsPbBr₃ and CsPbI₃ exciton binding energy were measured to be ~72 meV^[69], 38 meV^[69] and 20 meV^[85]. Exciton binding energy can also be tuned by varying organic cations. CsPbX₃ has higher exciton binding energy than MAPbX₃ because of smaller effective mass of electrons and holes.^[86] Nevertheless, exciton binding energy of perovskites could be engineered from several to hundreds of meV via change of stacking, structure and cations,

etc.^[38] It provides huge opportunities to both high-performance devices and tailoring emission in weak and strong light-matter coupling regime. The perovskites with large binding energy, such as CsPbX₃, MAPbBr₃, MAPbCl₃, FAPbBr₃, FAPbCl₃ are potential for coherent and incoherent photonic sources.^[29, 69] On the other hands, the perovskites with small binding energy, such as MAPbI₃, MAPbI_xCl_{3-x}, are good candidates for solar cell devices in a need of free carriers.^[39, 87]

1.4 Optical Gain

In stimulated emission process of exciton or free carriers, one photon creates the emission of two photons through electron-hole recombination, which is the source of optical gain in semiconductors. Semiconductor optical gain g , united as cm^{-1} , describes the light amplification per length of semiconductor materials. As light waves propagate along an optical waveguide, the intensity exponentially increases with propagation length via amplitude of optical gain. Generally, semiconductor gain depends on dipole transition moment and states distribution of electron and hole near the Fermi level, which is quite similar to optical absorption. It means that semiconductors such as perovskites owning large absorption coefficient potentially also have large optical gain. On the other hands, the propagating light waves can damp via absorption, scattering and leakages, which is so-called optical losses. In semiconductor microcavities, optical losses are mainly from phonon scattering, non-radiative recombination, edge scattering during propagation process and field leakage from cavity facets. The ultra-low density of defect states inside perovskites promises relatively lower optical loss in perovskite waveguides.

To reach lasing status, modal optical gain of microcavities needs to overcome optical losses. The net optical gain, described by the offset between gain and loss, can be measured

by variable stripe length technique. In this method, cylindrical spot is used as excitation source and emission intensity is measured with a function of the length of excitation laser spot. The stimulated emission process of perovskite was firstly observed via transition absorption spectroscopy with a negative absorbance near to band gap. The optical gain, or the upper limit of net modal gain is reported to be $\sim 3,200 \text{ cm}^{-1}$ for perovskite thin film, which is close to single crystalline GaAs as a result of large absorption coefficient.^[88] Using variable stripe length technique, the net modal gain near the threshold are measured to be $\sim 250 \text{ cm}^{-1}$ ^[60], 120 cm^{-1} ^[89], 450 cm^{-1} ^[65] for MAPbI₃ film, MAPbI₃ nanocrystals, CsPbBr₃ nanocrystals, respectively. Although there is no definite value, the gain of MAPbBr₃ is expected higher than that of MAPbI₃. These optical gain values obtained from the respective methods are comparable favorably with those for colloidal QDs and conjugated polymer thin films.^[90, 91] The great optical gain and low defect states of perovskites strongly promise high performance laser devices in the future.

Section 2. Perovskite Microcavities and Microlasers

Since the first demonstration of ASE from solution-processed perovskite thin films, room-temperature perovskite lasers have been realized in NWs, NPs and QDs, *etc* (**Figure 3a**). The composition, crystalline structure and morphology of perovskite nanostructures can be controlled by growth proceeding for divergent applications. Single crystalline perovskite nanostructures have uniform shapes, smooth surfaces and specified facets. With the smooth structural facets serving as mirrors and perovskite crystals themselves serving as gain media (see Figure 3a), the NWs and NPs naturally form active F-P and whispering gallery mode (WGM) cavities (**Figure 3b-c**). For example, photons propagate along the axial direction and oscillate between the two end-facets of the NW. When the wavelength of photons satisfies the

resonance conditions of microcavities (so-called resonance mode), the photon modes is substantially enhanced; otherwise it is surpassed.^[92] In addition to the F-P cavities geometry, polygonal nanoplatelets or spheres are of great interest as they can naturally form WGM cavities (**Figure 3c**) and provide total internal reflection, leading to superior light confinement. In WGM cavities, light can be trapped within a sphere or ring of gain material with higher refractive index than the environment, providing relatively higher cavity quality factor (Q) than F-P cavity. Beyond the active semiconductor cavities, perovskite nanostructure can only serve as gain media and be coupled with other passive optical cavities including Bragg reflector F-P cavity and photonic crystal cavities to form laser devices (**Figure 3d**). In the following discussion, we will summarize different types of perovskite structures and lasers ranging from two-dimensional NPs, one-dimensional NWs to zero-dimensional QDs.

2.1 Two-Dimensional Nanoplatelets: Whispering-Gallery-Mode Lasers

Two-dimensional perovskite structures such as NPs and microdisks (MDs) have been demonstrated with excellent WGM lasing property.^[93-95] Following ASE and lasing of thin perovskite film, the first perovskite microlaser was realized in high quality $\text{MAPbI}_{3-x}(\text{Cl/Br})_x$ polygonal NPs fabricated by two-step vapor-phase deposition method in 2014.^[66] Due to the intrinsic hexagonal crystalline structure, triangular or hexagonal-shape PbX_2 nanoplatelets were firstly obtained and followed by in-situ conversions into MAPbX_3 perovskite crystals. The shape of as-grown crystals remains, serving as WGM cavities. As shown in **Figure 4a**, room temperature lasing at ~ 780 nm was observed from the well-defined MAPbI_3 NPs when they were pumped by a fs-pulsed laser with a threshold of $\sim 37 \mu\text{J}/\text{cm}^2$ (pulse width: ~ 120 fs, repetition rate: 1 KHz). The lasing spectra coherence, evaluated via full width at half maximum (FWHM) of lasing peak is 0.9-1.2 nm. MAPbBr_3 with green emission exhibits

higher quantum yield, better stability and larger optical gain than MAPbI₃, leading to lower lasing threshold. For example, Liao *et al.* grew single-crystalline MAPbBr₃ square MDs using one-step method and obtained lasing at 557 nm.^[63] The lasing threshold is 3.6 $\mu\text{J}/\text{cm}^2$ (pulse width: 120 fs; **Figure 4b**). Their four side-facets constituted a built-in WGM micro-resonator with a spectra-coherence of 1.29 nm at room temperature. However, the hybrid inorganic-organic perovskites suffer from poor stability under atmosphere. As a contrast, pure inorganic perovskite CsPbX₃ not only show good stability but also higher quantum yield. As shown in **Figure 4c**, CsPbX₃ was synthesized using chemical vapor phase deposition on mica substrate via Van der Waals epitaxy. NPs with square shape and smooth surface aligned along mica crystalline axis.^[69] The absorption and PL clearly shows strong excitonic peak with FWHM of ~10-12 nm at room temperature, suggesting the large exciton binding energy in inorganic CsPbX₃ perovskites. The lasing emission could be tuned throughout the whole visible regime as shown in Figure 4c (bottom panel). The lasing FWHM is ~0.14-0.16 nm, which is the highest among as-reported nanostructure semiconductor lasers and comparable with commercial lasers. The CsPbX₃ NPs laser also show low threshold of 2.0 $\mu\text{J}/\text{cm}^2$, which is comparable with other II-V semiconductor microlasers and smaller than MAPbX₃ with the same size. The remarkable lasing performance of CsPbX₃ holds important potential for developing integrated laser sources.

2.2 One-Dimensional Nanowires: Fabry-Pérot Nanowire Lasers

Attributing to ultra-compact physical sizes, highly localized coherent output, and efficient waveguide, semiconductor NWs are promising building blocks for fully integrated nanoscale photonic and optoelectronic devices. One of the main obstacles limiting potential applications of semiconductor NW lasers is the high threshold carrier density required for

lasing.^[9, 96, 97] It is thus anticipated that perovskites NW lasers would show more intriguing features than their bulk counterparts by integrating various advantages of perovskites and one dimensional materials. As shown in **Figure 5a**, Zhu *et al.* reported the first demonstration of perovskite nanowire lasers.^[67] Through adopting one-step wet chemical method, high quality MAPbX₃ perovskite NW F-P cavity was fabricated, which exhibits ultralow lasing thresholds (220 nJ cm⁻²), high coherence (laser pulse width: 100 fs @ 250 kHz; 0.24 nm @ 750 nm) and broad tunability covering the near-infrared to visible wavelength region. Such exceptional lasing performance is believed to originate from long carrier lifetime and low non-radiative recombination rates of rectangular perovskite NWs in cross-section. After that, Xing *et al.* synthesized free-standing perovskite NWs through two-step vapor-phase synthesis,^[98] which shows optically pumped lasing with near-infrared wavelength of 777 nm, low threshold of 11 μJ cm⁻², and lasing spectra coherence of 1.9 nm (laser pulse width: 120 fs; **Figure 5b**). Although they exhibit excellent performance, their intrinsic instability is still big concerns for the hybrid perovskite NWs.^[99, 100] Aiming to solve the optical and thermal stabilities problems of perovskite NW lasers, Fu *et al.* recently report a low-temperature solution growth of single crystal FAPbX₃ NWs (**Figure 5c**).^[62] Room temperature near-infrared lasing (~820 nm) was demonstrated with durable lasing for over 10⁸ excitation cycles. Meanwhile, Eaton *et al.* reported ultra-stable pure-inorganic CsPbBr₃ perovskite NW lasers worked in ambient and vacuum condition. The CsPbBr₃ NW lasing lasted even after 10⁹ excitation cycles with low threshold of 5 μJ cm⁻² and excellent lasing spectra coherence of ~ 0.5 nm. (**Figure 5d**).^[61]

2.3 Zero-Dimensional Quantum Dots Laser

Nanocrystal QDs are attractive materials as laser media because of their size-tunable emission, well-separated delta function-like density of states, large optical oscillator strength,

and the flexibility afforded by colloidal synthesis, which promises a low-threshold and temperature-insensitive optical gain.^[11, 101-104] Perovskite QDs in particular, such as CsPbX₃ have ushered the advantages of perovskite materials into the realm of quantum confinement. Perovskite QDs exhibit narrow full widths at half-maximum (FWHM) and remarkably high PLQYs (approximately >70%) with emission tunable over a very broad spectral window, as shown in **Figure 6a**.^[65] The net gain value of CsPbBr₃ QDs film is $\sim 450 \text{ cm}^{-1}$, promising for lasing devices. For example, using cubic-shaped colloidal CsPbX₃ QDs with a mean size of $\approx 9\text{--}10 \text{ nm}$, Professor H. D. Sun's group demonstrated room temperature amplified of spontaneous emission in the visible spectral range using CsPbX₃ NQ thin films (470–620 nm) as shown in **Figure 6c**.^[105] As shown in **Figure 6b**, Yakunin *et al* fabricated CsPbX₃ QDs capped with oleylamine and oleic acid as ligand.^[65] Through coated QDs onto silicon sphere, WGM lasing from 440-700 nm was demonstrated with low thresholds down to $5 \mu\text{J cm}^{-2}$ (400 nm @ 100 fs).^[65] Pan *et al.* synthesized CsPbBr₃ QDs by using an inorganic–organic hybrid ion pair as the capping ligand.^[106] This passivation approach gives rise to high PLQY (up to 70%) of perovskite QDs with unprecedented operational stability in ambient conditions (60±5% lab humidity). More importantly, passivated perovskite QD films demonstrated remarkable photostability under continuous pulsed laser excitation in ambient conditions for at least 34 h (corresponds to 1.2×10^8 laser shots), substantially exceeding the stability of other colloidal QD systems in which ASE has been observed. Despite their favorable properties, application of QDs in lasing is hindered by extremely short optical gain lifetimes limited by nonradiative multicarrier Auger decay.^[107] It is essential to control Auger recombination towards the realization of real-life QD-based lasing technologies. Park *et al.* offer practical strategies for suppression of Auger recombination via “interface engineering” in core/shell structures.^[108] The suppression of Auger recombination in the sample with a

smooth (alloyed) interface results in a notable improvement in the optical gain performance manifested in the reduction of the threshold for amplified spontaneous emission and the ability to produce dual-color lasing involving both the band-edge (1S) and the higher-energy (1P) electronic states. It is of great importance for the realization of real-life QD-based lasing technologies.

2.4 Solution Preceding Film and Photonic Laser

In addition to above perovskite nanostructure laser with active cavity, cavity-free solution processed perovskite films with large optical gain, can be directly integrated into various cavity resonators, showing great promise for the realization of on-chip coherent light sources. Meanwhile, the ease of fabrication greatly relieves the requirements of lasers. Their low temperature solution processing property is highly compatible with various substrates such as silicon based electronics and flexible polymer substrates. Optical gain properties of low temperature solution-processed perovskite polycrystalline films were first reported by Xing *et al.* (**Figure 7a**).^[60] Tunable robust amplified spontaneous emission from 400-800 nm were found in $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$ and their mixtures) with striking low threshold of $\sim 12 \mu\text{J cm}^{-2}$. Their high performance stems from the low bulk defect density of $\text{CH}_3\text{NH}_3\text{PbX}_3$. Followed after this work, Deschler *et al.* utilized low temperature solution processed method to obtain high quality $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films with photoluminescence quantum efficiency of 70% (**Figure 7b**).^[49] By embedding the polycrystalline $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films between a dielectric mirror and evaporated gold top mirror, room temperature vertical cavity laser could be realized with threshold of $0.2 \mu\text{J/pulse}$. Apart from vertical FP cavity perovskite laser, whisper gallery mode perovskite laser could be achieved by coupling perovskite active medium onto a whisper gallery resonator. Sutherland *et al.* utilized atomic layer deposition

technique to deposit a thin layer of $\text{CH}_3\text{NH}_3\text{PbI}_3$ films onto a silica sphere and successfully achieved whisper gallery mode lasing at 80 K (**Figure 7c**).^[89] The feasibility of lasing in perovskite film by nanosecond pulse excitation strongly indicates the high quality optical gain in perovskite. In addition to passive FP resonator and WGM resonator, photonic crystals could be another kind of ideal resonators to achieve high performance lasing of solution processed perovskite films. Chen *et al.* coupled the solution processed $\text{CH}_3\text{NH}_3\text{PbI}_3$ films into a two dimensional photonic crystal and successfully achieved single mode lasing with low threshold of $68.5 \pm 3.0 \mu\text{J cm}^{-2}$ (**Figure 7d**).^[109] Through evaporating perovskite thin film onto photo-resist grating structure, Saliba *et al.* utilized low threshold and tunable distributed feedback lasing from 770 to 793 nm.^[110] The lasing threshold is $\sim 0.32\text{-}2.11 \mu\text{J cm}^{-2}$ (pulse width: ~ 1 ns). Furthermore, the approach promises the scalability of two-dimensional multi-element pixelated array of microlasers, which finds crucial applications in high brightness display and 3D modulated projection. However, solution processed perovskite films usually suffer from polycrystalline nature and low quantum efficiency, which dramatically restricts the performance of perovskite passive cavity laser. To improve the quality of solution processed films could be a crucial step towards high performance large area and low cost laser.

Section 3 Arrayed Micro-/Nano-Lasers

Apart from individual perovskite nanolaser, high-quality laser arrays could be more practical towards low cost, large area light emitting and optoelectronic applications. Integrated small laser array devices are important for scale-up large area, high power laser sources. Combining micro- and nano- fabrication and template methods, perovskite nanoplatelet arrays are designed, which has uniform shape in large area (~ 1 cm). Liu *et al.* reported a bottom-up Van der Waals epitaxy synthesis of $\text{CH}_3\text{NH}_3\text{PbI}_3$ microplatelet arrays on BN

(boron nitride) patterned films (see **Figure 8a**).^[111] Millimeter scale of hexagonal shaped two-dimensional crystals is patterned using a standard photolithography and etching proceeding. Using a two-step vapor phase method, PbI_2 with hexagonal crystalline structure is selected to grow on the two-dimensional crystals and then converted into MAPbI_3 . Furthermore, the emission properties of perovskite arrays, such as quantum yield and lifetime, could be controlled by using different substrates. These perovskite crystals serve as WGM microcavities due to their typical hexagonal shape. WGM lasing from the perovskite platelet was observed at room temperature with Q -factor as large as 1210 and a low threshold of $11 \mu\text{J}/\text{cm}^2$. Single mode lasing can be achieved by shortening the size of the cavity or through breaking the symmetry of the cavity. In addition to perovskite microcavity arrays, Wang *et al.* successfully achieved periodic nanolaser arrays by position a perovskite nanobelt onto a silicon grating.^[112] The lasing comes from the suspended parts which support the high quality resonances. High performance lasing with low threshold of $4.2 \mu\text{J}/\text{cm}^2$ can be observed in an air gap as narrow as 420 nm, demonstrating a high density of nanolaser arrays of about 1250 per millimeter. Feng *et al.* demonstrate a “liquid knife” strategy to regularly split perovskite precursor liquid and locate liquid domains by using wettability-mediated micro-pillar-structured (see **Figure 8b**).^[113] The crystalline structure, quantum yield and emission wavelength of each perovskite unit is almost the same. These fabricated patterning single-crystalline perovskite microplates can be served as high-performance lasers. Beyond the lasers, Wang *et al.* show that large arrays of lead iodide microplates can be grown from an aqueous solution through a seeded growth process and can be further intercalated with methylammonium iodide to produce perovskite crystals. They also demonstrate that perovskite crystals can be selectively grown on pre-patterned electrode arrays to create independently addressable photodetector arrays and functional field effect transistors.^[112]

Nevertheless, the fabrication of perovskite array by photolithography or electron beam lithography still encounters serious problems because the materials is unstable when they are exposed to those widely-used photoresist and lift-off solution. Carefully design of lithography proceeding will be helpful.

4. Conclusions and Challenges

To conclude, the concept article has discussed the recent development and research progress of metal halide perovskite based laser sources. We have introduced the emergence of high performance optically driven perovskite laser sources operated over ultra-violet to near-infrared regime. Generally, metal halide perovskite materials own significant advantages for photonic sources such as low-cost fabrication proceeding, flexible structure, high absorption coefficient and tunable emission etc. Perovskite lasers have become a fruitful research field towards practical applications. The recent studies on structure engineering, optical properties and device development of perovskites have led to a variety of promising work in both coherent and incoherent light sources.^[66, 67, 69]

Beyond these achievements, challenges remain in metal halide perovskite laser devices. Firstly, similar as in perovskite solar cells, the poor stability of perovskite under atmosphere and moisture and the toxicity of Pb are two serious issues for perovskite photonic sources. Strict encapsulation could be a solution to reduce atom and moisture exposure. It has been reported that the stability can be improved by element doping or by cladding of thin-layered material to isolate air and moisture. Since the devices are encapsulated to avoid toxic Pb directly exposed to human users, the recycle technology of Pb materials will be more helpful. Another concern is the poor device stability under intense field excitation. Vacuum or N₂ encapsulation may provide a solution. Secondly, the photo-physics of perovskite materials,

such as carrier dynamics is another interesting issue. In the big family of perovskites, the exciton and carrier behaviors exhibit big differences with varying the organic and inorganic units. Particularly the hybrid perovskite system could be not simply understood using the theory established by either inorganic semiconductor or organic semiconductors. A deep understanding of fundamental optical excitation mechanism of the hybrid perovskites is necessary. Furthermore, in lead halide perovskite family, there are a lot of crystals with large exciton binding energy, which promises the future of low-threshold perovskite exciton-polariton lasing. For example, solution processed two-dimensional layered perovskites $\text{C}_5\text{H}_6\text{CH}_2\text{NH}_2\text{PbI}_4$ exhibits significant exciton-polariton effect at room temperature. With more efforts on sample fabrication, it is promising to achieve polariton lasing at room temperature in these structures. Lastly, realizing electrically pumped laser emission is the ultimate goal, although there is a long way to go. Therefore, at present stage, using optically driven method to explore some fundamental properties of perovskite, including its stability, optical gain, threshold and so on, appears especially important and essential. Nevertheless, the optical and opto-electric studies on perovskite should be a fruitful research field and needs more efforts from worldwide researchers.

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Figure and Captions

Figure 1| Crystalline Structure of Lead Halide Perovskites. (a) Schematic of unit cell and crystalline structure of typical perovskite structures. In unit cell (upper panel), A, M, X locates at eight corners, body centre and six face centres of unit cell, respectively. (b) Crystalline structure of three-dimensional perovskite with chemical formula of AMX_3 . A is $CH_3NH_3^+$, $CH_2=CH_2^+$, Cs^+ , *etc.* (c) Crystalline structure of two-dimensional layered perovskite with chemical formula of A_2MX_4 . A is $C_5H_6CH_2NH_2^+$, *etc.*

Figure 2| Electronic Structure and Bandgap. Electronic structures (a) and projected density of states (b) of $\text{CH}_3\text{NH}_3\text{PbX}_3$ perovskite obtained by first-principles density functional theory (DFT) calculation. The band edge states are dominated by Pb p-orbitals, s-orbitals and X p-orbitals. The orbitals are indicated by red arrows. The electronic states of M located far below band edge. ^[72] (c) Schematics of band gap energies of MAPbX_3 , FAPbX_3 , CsPbX_3 , and CsSnX_3 . These data are obtained by previous literatures. ^[42, 60, 65, 68, 114]

Figure 3| Different Types of Perovskite Structures and Cavities. (a) Low dimensional perovskite structures from zero-dimensional (0-D) nanocrystals, one-dimensional nanowires and nanorods (1-D), two-dimensional (2-D) nanoplates towards three dimensional (3-D) bulk crystals. (b) Schematic of small perovskite lasers based on whispering-gallery-mode cavity laser formed by square/hexagonal platelet and perovskite coated spheres. (c) Nanowire laser serving as Fabry-Pérot (FP) laser. (d) Photonic crystal and distributed Bragg reflective (DBR) cavity lasers.

Figure 4| Perovskite Whispering-Gallery-Mode (WGM) Perovskite Lasers. (a) Near-infrared WGM laser using $\text{CH}_3\text{NH}_3\text{PbI}_3$ nanoplatelet grown by two-step vapor-phase deposition method.^[66] The triangular and hexagonal nanoplates formed active WGM cavity (upper panel). Clear lasing peak from WGM mode can be resolved above lasing threshold (below panel). The output-input intensity curve show “S” shape from linear spontaneous emission, superlinear amplified spontaneous emission towards linear full lasing status. The lasing threshold is $\sim 37 \mu\text{J cm}^{-2}$. The full width at half maximum (FWHM) of lasing peak is 1.2 nm . **(b)** $\text{CH}_3\text{NH}_3\text{PbX}_3$ WGM laser working from ~ 420 to 790 nm through varying halide composition. ^[63] **(c)** High quality CsPbX_3 WGM laser over the whole visible spectra regime. (left panel) The square CsPbX_3 nanoplatelets are grown by one-step chemical vapor phase deposition method. The FWHM of lasing peak is $\sim 0.14\text{-}0.15 \text{ nm}$ (right panel). The threshold is $\sim 2.0 \mu\text{J cm}^{-2}$.^[69]

Figure 5| Perovskite Fabry-Perot (F-P) Nanowire Lasers. (a) $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbBr}_3$ nanowire fabricated by two steps chemical vapor phase deposition (left panel). The nanowires serve as F-P lasers (right, upper panel). Above lasing threshold, coherent emission is out-coupled from the two end-facets. The lasing wavelength can be tuned from 546 to 773 nm by varying halide composition (right, bottom panel).^[67] (b) $\text{CH}_3\text{NH}_3\text{PbX}_3$ nanowire laser fabricated by one-step solution method with lasing mode between 500 to 780 nm. The laser show high spectra coherence with FWHM of ~ 0.23 nm at 520 nm and ~ 0.22 nm at 780 nm.^[98] (c) Stable CsPbX_3 nanowire laser using one-step vapor-phase deposition method. The lasing threshold is $\sim 5.0 \mu\text{J cm}^{-2}$ and lasing peak FWHM is ~ 0.5 nm. The laser can work effectively under 10^9 and 4×10^8 pulse shot nitrogen and atmospheres.^[62] (d) FAPbX_3 nanowire lasers with tunable emission peak around 550 to 700 nm. The lasing threshold is and FWHM of lasing peak is 0.55 nm (402 nm, 150 fs, 240 Hz). The laser can work effectively under 6×10^8 pulse shot under nitrogen.^[61]

Figure 6| Perovskite Quantum Dots Lasers. (a) CsPbX₃ quantum dots fabricated by solution methods.^[65] (b) Net gain of CsPbX₃ quantum dots film measured by strip-length method. The net gain is around $\sim 450 \text{ cm}^{-1}$.^[65] (c) Amplified spontaneous emission of CsPbX₃ quantum dots thin films. The threshold is $\sim 20 \mu\text{J cm}^{-2}$.^[64] (d) WGM lasing from CsPbX₃ quantum dots coated silicon microsphere resonator (diameter: $\sim 15 \mu\text{m}$). The lasing spectral coherence is $\sim 0.2 \text{ nm}$.^[65]

Figure 7 | Perovskite Laser Coupled with Passive Optical Micro-cavities. (a) Low temperature amplified spontaneous emission (ASE) of $\text{CH}_3\text{NH}_3\text{PbX}_3$ thin film spin-coated on Si substrate.^[60] **(b)** Lasing from thin film embedded in two distributed Bragg mirrors.^[49] The threshold is ~ 0.2 μJ per pulse. **(c)** Lasing from $\text{CH}_3\text{NH}_3\text{PbX}_3$ thin film coated on silica sphere.^[89] The lasing threshold is ~ 75 $\mu\text{J cm}^{-2}$. **(d)** Perovskite thin film spin-coated onto photonic crystals cavity formed by EBL patterned periodical array. Pixelated perovskite laser array is also fabricated.^[109]

Figure 8| Perovskite Laser Arrays. (a) $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite WGM laser arrays. PbI_2 arrays are deposited on two dimensional crystals micro-arrays by vapor-phase deposition and then transfer to $\text{CH}_3\text{NH}_3\text{PbI}_3$ in vapor phase. The lasing threshold is $\sim 11 \mu\text{J cm}^{-2}$ (400 nm, 150 fs, 1KHz).^[111] **(b)** $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite WGM laser arrays fabricated by “liquid knife” method.^[113]

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