

The strategies for preparing blue perovskite light-emitting diodes

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Abstract: Metal halide perovskites have attracted tremendous interest due to their excellent optical and electrical properties, and they find many promising applications in the optoelectronic fields of solar cells, light-emitting diodes, and photodetectors. Thanks to the contributions of international researchers, significant progress has been made for perovskite light-emitting diodes (Pero-LEDs). The external quantum efficiencies (EQEs) of Pero-LEDs with emission of green, red, and near-infrared have all exceeded 20%. However, the blue Pero-LEDs still lag due to the poor film quality and deficient device structure. Herein, we summarize the strategies for preparing blue-emitting perovskites and categorize them into two: compositional engineering and size controlling of the emitting units. The advantages and disadvantages of both strategies are discussed, and a perspective of preparing high-performance blue-emitting perovskite is proposed. The challenges and future directions of blue Pero-LEDs fabrication are also discussed.

Key words: perovskite; blue; light-emitting diodes

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1. Introduction

The metal halide perovskites have a general chemical formula of ABX_3 : A is a monovalent organic or inorganic cation, e.g., $CH_3NH_3^+(MA^+)$, $CH(NH_2)_2^+(FA^+)$, Cs^+ , Rb^+ ; B is a divalent metal cation, e.g., Pb^{2+} , Sn^{2+} ; X is a halide anion, e.g., Cl^- , Br^- , I^- . The perovskites have attracted tremendous interests due to their excellent properties such as easy solution-based fabrication process, high absorption coefficient, tunable energy bandgaps, narrow emission linewidths, and long exciton diffusion length^[1–3]. These outstanding properties lead perovskites to be used in a wide range of optoelectronic applications, including solar cells, light-emitting diodes (LEDs), and photodetectors. In this minireview, we will focus on perovskite light-emitting diodes (Pero-LEDs), in which perovskite is used as an emitting layer. In the past few years, the Pero-LEDs have shown great potential in applications like lighting, displays, and light communication.

In 2014, the first bright and room-temperature operative Pero-LEDs were fabricated using $MAPb_{1-x}Cl_x$ (near-infrared) and $MAPbBr_3$ (green) as emitting layers, which obtained an external quantum efficiencies (EQEs) of 0.76% and 0.1%^[1], respectively. Then, several strategies were demonstrated to enhance the efficiency of Pero-LEDs, including compositional engineering, morphology controlling, and device structure engineering^[2–7]. Recently, the EQEs of green, visible red, and near-infrared emitting Pero-LEDs have all exceeded 20%, reaching 20.3%^[7], 21.3%^[8], and 21.6%^[6], respectively. However, the efficiency growth of blue Pero-LEDs lags behind their counterparts, as shown in Table 1, the EQE of

deep-blue (440–470 nm), pure blue (470–480 nm), and blue-green (480–510 nm) emitting Pero-LEDs is lower than 3%, 6%, and 11% respectively^[9]. Blue is one of the three primary colors, and the blue LEDs play an essential role in displays and white lighting^[10]. In other words, developing high-performance blue Pero-LEDs takes a lot of effort.

In this review, the recent progress of blue Pero-LEDs, especially for the strategies of preparing the blue perovskite emitting layer, are summarized. We categorize the strategies into two: compositional engineering and size controlling of the emitting units. Compositional engineering, including A-, B-, and X-site doping and lead-free perovskites, is the simplest and most effective strategy to tune the bandgap (emitting color) of perovskites^[11, 12]. Size control of the emitting units could be realized directly by synthesizing nanoplates (NPs) and quantum dots (QDs)^[13, 14]. It could also be realized by forming low-dimensional (2D and quasi-2D) perovskites (forming small emitting perovskite units by cutting the 3D emitting center with the long-chain organic ligands)^[15, 16] or reducing the thickness of perovskite films to the nanoscale^[17]. Once the size of perovskite emitting crystals were reduced to the nanoscale, the bandgap of perovskites will be enlarged owing to the quantum-confined effect, and the emitting color will be blue-shift^[13]. Here the advantages and disadvantages of both methods to prepare blue-emitting perovskites will be discussed, and we will also give a perspective of preparing high-performance perovskites emitting layers and the corresponding Pero-LEDs.

2. The strategies to prepare blue-emitting perovskites

To prepare the blue-emitting perovskites, researchers have proposed a mass of methods. Fundamentally, these meth-

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Table 1. Performance summary of blue-emitting perovskites and the corresponding Pero-LEDs.

Strategies	Perovskite	PL peak (nm)	EL peak (nm)	Lv_{\max} (cd/m ²)	EQE_{\max} (%)	Year	Ref.
Compositional engineering	Film	MAPb(Br _{1-x} Cl _x) ₃	408–535	475	2	3 * 10 ⁻⁴	2015 Kumawat <i>et al.</i> [11]
	Film	MAPb(Br _{1-x} Cl _x) ₃	428–543	427–570	–	–	2015 Sadhanala <i>et al.</i> [12]
	Film	Cs ₁₀ (MA _{0.17} FA _{0.83}) _{100-x} PbBr _{1.5} Cl _{1.5}	–	475	3567	1.7	2017 Kim <i>et al.</i> [38]
	Film	CsMn _y Pb _{1-y} Br _x Cl _{3-x}	–	466	245	2.12	2018 Hou <i>et al.</i> [39]
	Crystal	Cs ₂ SnCl ₆ :Bi	455	–	–	–	2018 Tan <i>et al.</i> [28]
Size control of the emitting units	QDs	CsPbBr ₃	470–515	–	–	–	2015 Song <i>et al.</i> [13]
	NPs	(PEA) ₂ PbBr ₄	407	410	–	0.04	2016 Liang <i>et al.</i> [15]
	NPs	2D n (MAPbBr ₃), $n = 1/3/5$	436/456/489	432/456/492	1/2/8.5	0.004/0.024/0.2	2016 Kumar <i>et al.</i> [16]
	QDs	CsPbBr ₃	460	–	–	–	2016 Lu <i>et al.</i> [49]
	Film	(EA) ₂ MA _{n-1} Pb _n Br _{3n+1}	473, 485	473, 485	200	2.6	2017 Wang <i>et al.</i> [37]
	NPs	CsPbBr ₃	442–459	480	25	0.1	2018 Yang <i>et al.</i> [32]
	Film	PEA ₂ CsPb ₂ Br ₇ @Cs ₄ PbBr ₆	–	500	3259	4.51	2018 Shang <i>et al.</i> [31]
	Film	PA ₂ (CsPbBr ₃) _{n-1} PbBr ₄	425–525	505	~10 ⁴	3.6	2018 Chen <i>et al.</i> [29]
	NPs	2D CsPbBr ₃	432–497	464	38	0.057	2018 Bohn <i>et al.</i> [14]
	Film	PEA ₂ A _{n-1} Pb _n Br _{3n+1}	480	490	2480	1.5	2018 Xing <i>et al.</i> [30]
	QDs	CH ₃ NH ₂ PbBr ₃	440	453	32	–	2018 Zhang <i>et al.</i> [50]
	Film	PEA ₂ Cs _{n-1} Pb _n Br _{3n+1}	–	484	45	0.13	2019 Zou <i>et al.</i> [34]
	Film	PA ₂ (CsPbBr ₃) _{n-1} PbBr ₄	488	492	4359	1.45	2019 Ren <i>et al.</i> [36]
	NPs	(PEA) ₂ PbBr ₄	408	410	147.6	0.31	2019 Deng <i>et al.</i> [40]
	Film	PBABr _y (Cs _{0.7} FA _{0.3} PbBr ₃)	–	483	54	9.5	2019 Liu <i>et al.</i> [17]
	Film	P-PDA,PEACs _{n-1} Pb _n Br _{3n+1}	–	465	211	2.6	2019 Yuan <i>et al.</i> [41]
	Compositional engineering and Size control of the emitting units	QDs	CsPb(Br _{1-x} Cl _x) ₃	420–500	455	742	0.07
NCs		CsPbBr _{1.5} Cl _{1.5}	470	480	8.7	0.0074	2016 Li <i>et al.</i> [42]
QDs		CsPbBr _{1.5} Cl _{1.5} /CsPbBr _{2.4} Cl _{0.6}	450/459	445/495	2673/2652	1.38/1.13	2016 Deng <i>et al.</i> [23]
QDs		CsPb(Br _{1-x} Cl _x) ₃	–	490	35	1.9	2016 Pan <i>et al.</i> [43]
QDs		Cs ₃ Bi ₂ Br ₉	410	–	–	–	2017 Leng <i>et al.</i> [44]
NCs		CsPbBr _x Cl _{3-x}	–	469	111	0.5	2018 Gangishetty <i>et al.</i> [22]
Film		BA ₂ Cs _{n-1} Pb _n (Br/Cl) _{3n+1}	464/486	465/487	962/3340	2.4/6.2	2018 Vashishtha <i>et al.</i> [45]
QDs		(Rb _{0.33} Cs _{0.67}) _{0.42} FA _{0.58} ⁻ PbBr ₃ /(Rb _{0.33} Cs _{0.67}) _{0.42} ⁻ FA _{0.58} ⁺ PbBr _{1.75} Cl _{1.25}	500/476	502/466	10 ³ /40	3.6/0.61	2018 Meng <i>et al.</i> [33]
QDs		MA ₃ Bi ₂ (Cl/Br) ₉	422	–	–	–	2018 Leng <i>et al.</i> [27]
Film		PEA ₂ (CsPbBr _{2.1} Cl _{0.9}) _{n-1} PbBr ₄	–	480	3780	5.7	2019 Li <i>et al.</i> [42]
Film		PEA ₂ (Rb _{0.6} Cs _{0.4}) ₂ Pb ₃ Br ₁₀ /PEA ₂ (Rb _{0.4} Cs _{0.6}) ₂ Pb ₃ Br ₁₀	–	475/490	–	1.35/1.48	2019 Jiang <i>et al.</i> [26]
NCs		CsPb(Br/Cl) ₃	461	463	318	1.2	2019 Ochsenbein <i>et al.</i> [46]
QDs		Rb _x Cs _{1-x} PbBr ₃	460–500	490/464	183/63	0.87/0.11	2019 Todorovic <i>et al.</i> [25]
Film		POEA–CsPbBr _{1.65} Cl _{1.35}	468	468	122.1	0.71	2019 Tan <i>et al.</i> [35]
Film		CsPbBr ₃ :PEACl:2%YCl ₃	485	485	9040	11	2019 Wang <i>et al.</i> [9]
NCs		CsPb(Br/Cl) ₃	–	477	87	1.96	2020 Yang <i>et al.</i> [47]
QDs		CsPbCl _{0.99} Br _{2.01} :2.5%NiCl ₂	–	470	612	2.4	2020 Pan <i>et al.</i> [48]

NPs (nanoplates), NCs (nanocrystals), QDs (quantum dots), MA (methylamine), FA (formamidine), EA (ethylamine), BA (butylamine), PEA (phenylethylamine), PA (propylamine), PBA (phenylbutylammonium), P-PDABr₂ (polyammonium bromide [1,4-Bis(aminomethyl)benzene bromide]), POEA (2-phenoxyethylamine).

ods could be categorized into two basic aspects. One is enlarging the energy bandgap by replacing the elements of perovskite crystals. Due to the excellent tolerance of perovskite crystals, lots of elements could be used to form the stable perovskite crystals^[18, 19]. Recently, Bartel *et al.*^[20] reported a new tolerance factor to predict the stability of perovskite oxides and halides. They not only correctly predicted 92% of compounds as perovskite or non-perovskite for an experimental dataset of 576 ABX₃ materials, but also they generalized outside the training set for 1034 experimentally realized single and double perovskites (A₂BB'X₆) to identify the stability of

23 314 new double perovskites. According to their research, abundant stable perovskites could emit blue have not been studied by researchers. However, one of the fatal drawbacks is that non-homogeneous phase distribution and phases segregation would be likely inevitable if the components of perovskites are partly replaced^[11]. The other strategy is to reduce the size of perovskite crystals to create the quantum confined effect. When the size was reduced to the nanoscale, notably less than the exciton Bohr radius, the energy bandgap will increase and induce emitting peak shifting to the blue region, and this theory is widely applied in fabricating of the tra-

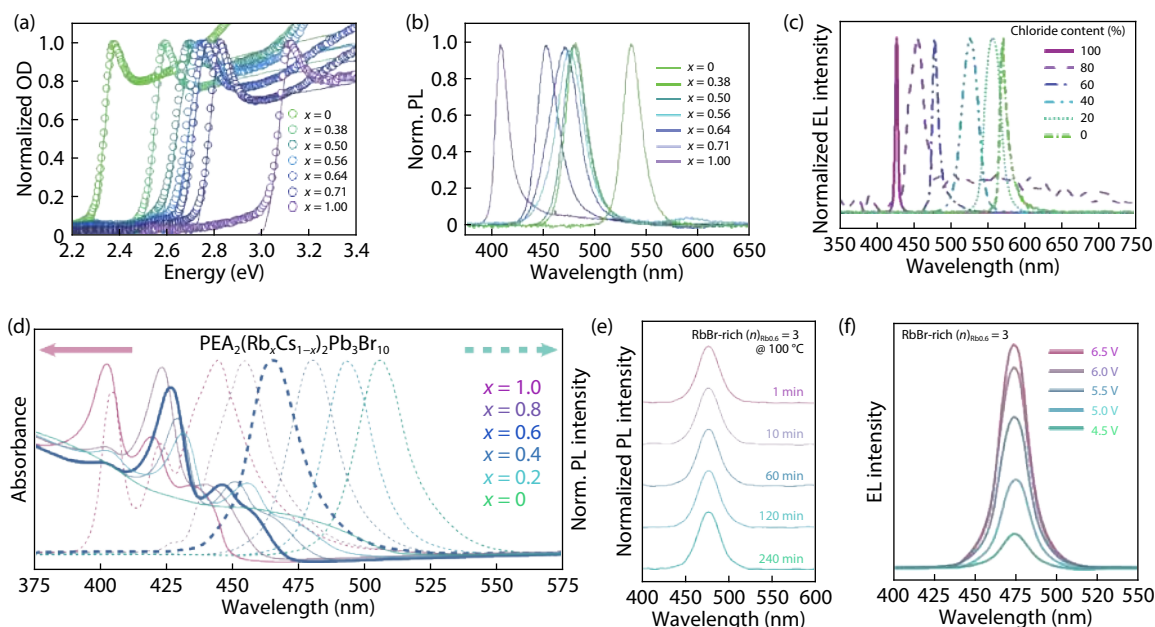


Fig. 1. (Color online) Blue-emitting perovskites prepared by composition engineering. (a) Normalized absorbance and (b) photoluminescence of $\text{MAPb}(\text{Br}_{1-x}\text{Cl}_x)_3$ ($0 \leq x \leq 1$). Reproduced with permission from Ref. [11]. Copyright 2015, American Chemical Society. (c) The curves of electroluminescence of Pero-LEDs based on $\text{MAPb}(\text{Br}_{1-x}\text{Cl}_x)_3$ ($0 \leq x \leq 1$). Reproduced with permission from Ref. [12]. Copyright 2015, American Chemical Society. (d) UV-vis absorbance and steady-state PL spectra of $\text{PEA}_2(\text{Rb}_x\text{Cs}_{1-x})_2\text{Pb}_3\text{Br}_{10}$ ($0 \leq x \leq 1$) perovskites. (e) The PL spectra evolution of $\text{PEA}_2(\text{Rb}_{0.6}\text{Cs}_{0.4})_2\text{Pb}_3\text{Br}_{10}$ perovskites after continuous thermal treatment (100°C) for different times. (f) The EL spectra of Pero-LEDs based on $\text{PEA}_2(\text{Rb}_{0.6}\text{Cs}_{0.4})_2\text{Pb}_3\text{Br}_{10}$ perovskites at different voltage bias. Reproduced with permission from Ref. [26]. Copyright 2019 Springer Nature.

ditional blue-emitting quantum dot (QD)-LEDs^[21]. Nevertheless, the disadvantages of this strategy are also apparent. Specifically, the electrical conductivity will decrease dramatically after adding the insulating organic ligands^[13, 22], and the size of crystals is hard to control and tend to be inhomogeneous when the crystals are synthesized to the nanoscale^[13, 23].

2.1. Compositional engineering

Generally, according to the tight-binding approximation, the bandgap of crystals will get widened if the elements are replaced by the ones in the smaller period of the same family^[24]. Hence, the mixing of halide anions was firstly applied to prepare blue-emitting perovskites. In 2015, Kumawat *et al.*^[11] firstly reported the blue emissive Pero-LEDs based on $\text{MAPbBr}_{1.08}\text{Cl}_{1.92}$. The bandgap changes when varying the ratio of Br^- and Cl^- . Fig. 1(a) shows that the absorption moves to higher energy with the increasing of chlorine concentration, indicating that the bandgap increases with the growth of chlorine fraction. Furthermore, the photoluminescence (PL) peaks of the corresponding perovskites cover the range from 408 to 535 nm, as shown in Fig. 1(b). Sadhanala *et al.* conducted similar research^[12], and the bandgap tuning range of the $\text{MAPb}(\text{Br}_x\text{Cl}_{1-x})_3$ ($0 \leq x \leq 1$) perovskites is $\sim 3.1\text{--}2.3$ eV. Fig. 1(c) shows that the electroluminescence (EL) peaks of Pero-LEDs based on such perovskites could be tuned from 427 to 570 nm by controlling the chloride content. At present, halogen doping is widely used as the most effective and simplest method for preparing blue-emitting perovskites.

However, using the simple halogen doping method to prepare the Pero-LEDs, the problem of phase segregation will be inevitable when the devices operated at high voltage. Hence, researchers developed alternative methods by A- or

B-site doping to control the bandgap of perovskites and stabilize the crystalline phases. Todorovic *et al.*^[25] reported a tunable and stable electroluminescence perovskite enabled by Rb doping of CsPbBr_3 nanocrystals (NCs), which could obtain tunable emission from 460 to 500 nm. Impressively, unlike the halide mixing, the Pero-LEDs based on Rb-doped perovskites achieved stable emission peaks at 464 and 490 nm with EQE_{max} of 0.11% and 0.87% respectively. The Rb-doped quasi-2D perovskites were also demonstrated by Jiang *et al.*^[26]. As shown in Fig 1(d), the PL peaks of $\text{PEA}_2(\text{Rb}_x\text{Cs}_{1-x})_2\text{Pb}_3\text{Br}_{10}$ could be tuned from 450 to 510 nm by controlling the ratio of Rb^+ and Cs^+ . Compared to the halogen-doped perovskites, the Rb-doped perovskites exhibit excellent spectral stability, in which both the PL peak position and the full width of half maximum (FWHM) changed negligibly after 4 h of annealing (Fig. 1(e)). And the corresponding Pero-LEDs obtained spectrally stable emission at 475 nm (Fig. 1(f)) and 490 nm based on $\text{PEA}_2(\text{Rb}_{0.6}\text{Cs}_{0.4})_2\text{Pb}_3\text{Br}_{10}$ and $\text{PEA}_2(\text{Rb}_{0.4}\text{Cs}_{0.6})_2\text{Pb}_3\text{Br}_{10}$, respectively.

Compared to the regulation of A- and X-site of perovskite crystals, B-site doping, and lead-free perovskites could own a stronger ability to adjust the bandgap and achieve deep-blue emission. Leng *et al.*^[27] reported a lead-free perovskite of $\text{Cs}_3\text{Bi}_2\text{Br}_9$ QDs, showing a deep-blue emission at 410 nm with a photoluminescence quantum yield (PLQY) up to 19.4%. Moreover, the emission range could be adjusted from 393 to 545 nm by incorporating with the halogen-doping method. Furthermore, they applied Cl-passivation to boost the PLQY of $\text{MA}_3\text{Bi}_2\text{Br}_9$ QDs to 54.1% at the wavelength of 422 nm in their later work. Tan *et al.*^[28] reported a bismuth (Bi)-doped lead-free perovskite of Cs_2SnCl_6 crystal with the outstanding anti-water stability, which could preserve 97.1% of the initial PL intensity after 120 min soaking.

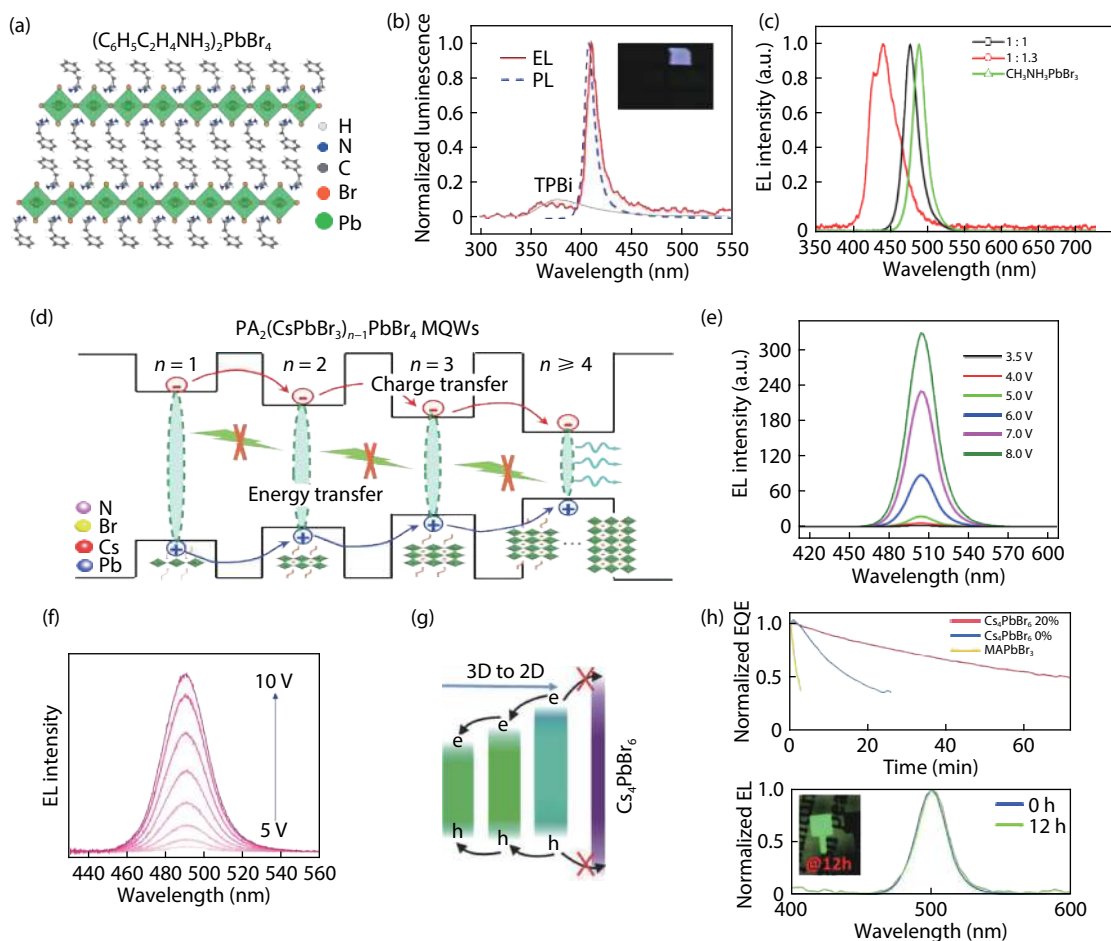


Fig. 2. (Color online) Blue-emitting perovskites prepared by forming the 2D and quasi-2D structure. (a) Crystal structure of 2-phenylethylammonium lead bromide, $(\text{PEA})_2\text{PbBr}_4$, which is a 2D layered perovskite, and (b) the corresponding PL and EL peaks located at 407 and 410 nm, respectively. The weak EL peak at 375 nm is from TPBi, consistent with its PL (gray curve). Reproduced with permission from Ref. [15]. Copyright 2016, American Chemical Society. (c) The EL spectra of Pero-LEDs based on the quasi-2D perovskites of $(\text{EA})_2\text{MA}_{n-1}\text{Pb}_n\text{Br}_{3n+1}$ (MA : EA = 1 : 0, 1 : 1, and 1 : 1.3 respectively). Reproduced with permission from Ref. [37]. Copyright 2017, American Chemical Society. (d) Schematic of charge carrier cascade in the quasi-2D perovskite of $\text{PA}_2(\text{CsPbBr}_3)_{n-1}\text{PbBr}_4$ MQWs, and (e) the EL spectra of corresponding Pero-LEDs under different voltage bias. Reproduced with permission from Ref. [29]. Copyright 2018, Elsevier Ltd. (f) The stable EL spectra of Pero-LED based on quasi-2D perovskite of $\text{PEA}_2\text{A}_{n-1}\text{Pb}_n\text{Br}_{3n+1}$ under different voltage bias. Reproduced with permission from Ref. [30]. Copyright 2018 Springer Nature. (g) The diagram of carriers transfer between perovskite quantum wells (2D) and bulk perovskite part (3D), the Cs_4PbBr_6 facilitate carriers centralization. (h) The stability test under 10 mA/cm² of the device with different amounts of Cs_4PbBr_6 additive and the traditional MAPbBr_3 devices, and the EL spectra curves of 0 and 12 h are almost completely coincident. Reproduced with permission from Ref. [31]. Copyright 2018, WILEY-VCH.

Furthermore, the optimized perovskite exhibits a deep-blue emission at 455 nm and a high PLQY close to 80%. Although such high PLQYs of lead-free deep blue-emitting perovskites have reported, there are still lacking studies of their application on LED devices, due to the poor-quality morphology of the perovskite film.

According to the summaries in Table 1, it is obvious that few papers have reported high EQE by using the strategy of compositional engineering, even though the PL emission of perovskites could easily be adjusted by this method. In other words, it is hard to fabricate the spectrally stable and high efficiency deep blue-emitting Pero-LEDs only by compositional engineering.

2.2. Size control of the emitting units

As the particle size decreases to the nanoscale, the continuous energy levels near the Fermi energy level will be divided^[24]. Hence, reducing the size of perovskite crystals in some dimensionality should be an efficient approach to en-

large the bandgap of perovskites. Recently, 2D/quasi-2D perovskites and the pre-synthesis NPs, NCs, and QDs are widely used to prepare blue-emitting perovskites.

The 2D/quasi-2D perovskites could have a general formula of $\text{L}_2(\text{ABX}_3)_{n-1}\text{BX}_4$, where L is a monovalent long alkyl chain, and n is the number of stacking perovskite units. The bandgap of perovskites could be tuned by controlling the n values. Liang *et al.*^[15] reported the first Pero-LED based on 2D perovskite, using $(\text{PEA})_2\text{PbBr}_4$ ($\text{PEA}^+ = \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_3^+$) as emitting layer (Fig 2(a)), which obtained an emission at 410 nm (Fig. 2(b)) and an EQE_{max} of 0.04%. By controlling the n values, Wang *et al.*^[37] reported a dual emission (as shown in Fig. 2(c), 473 and 485 nm) Pero-LEDs based on $(\text{EA})_2\text{MA}_{n-1}\text{Pb}_n\text{Br}_{3n+1}$, which achieved an EQE_{max} of 2.6%. However, it is hard to control the n values precisely, and multiple n values always exist in the quasi-2D perovskite crystals. Chen *et al.*^[29] studied the charge-transfer and energy-transfer (Fig. 2(d)) among crystals with different n values in quasi-2D Pero-LEDs. According to their research, four distinct emissions at 425,

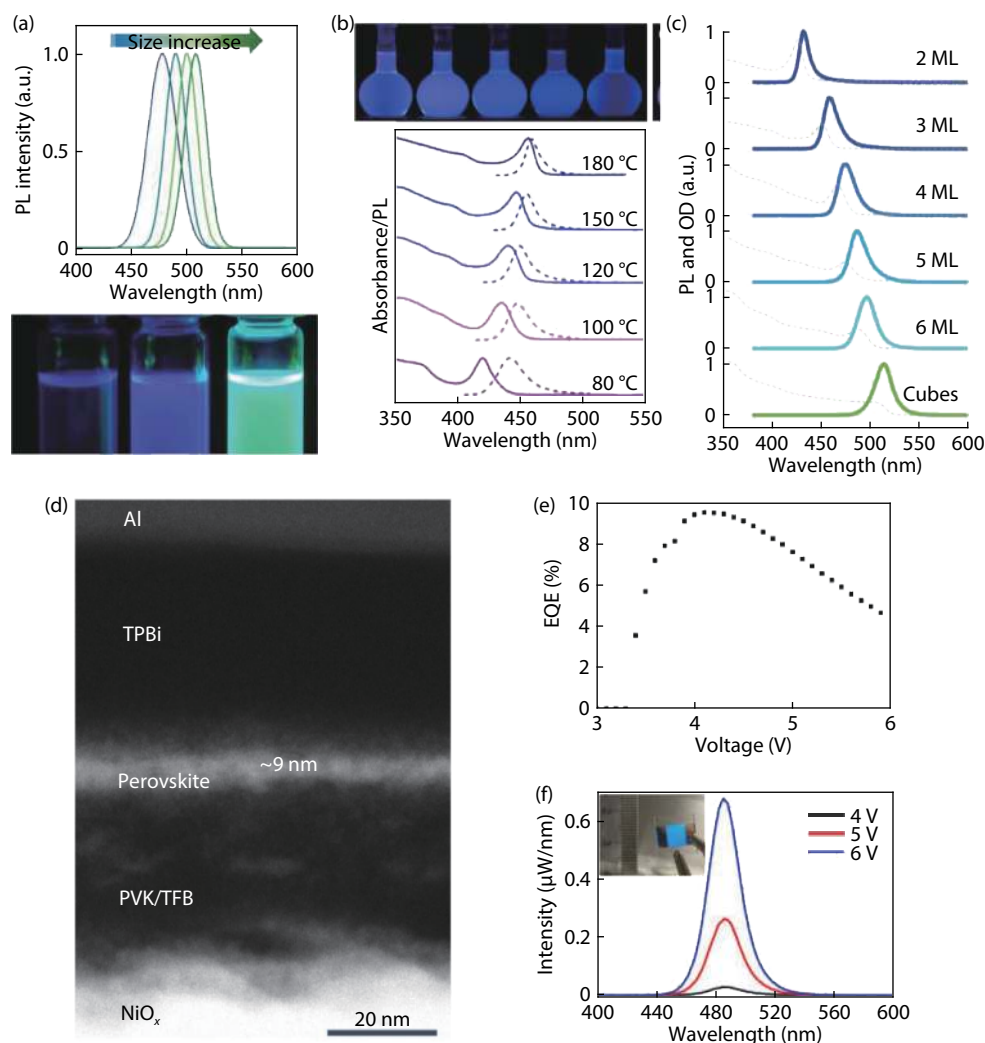


Fig. 3. (Color online) Blue-emitting perovskites prepared by controlling the size of perovskite crystals. (a) Size-dependent PL spectra and photographs of monodisperse perovskite CsPbBr_3 QDs. Reproduced with permission from Ref. [13]. Copyright 2015, WILEY-VCH. (b) Photographs of CsPbBr_3 NPs dispersion obtained at different temperatures and corresponding UV-vis absorption and PL emission spectra. Reproduced with permission from Ref. [32]. Copyright 2018, Elsevier Ltd. (c) PL (solid lines) and absorption (dashed lines) spectra of CsPbBr_3 NPs colloids for varying NPs thickness. Reproduced with permission from Ref. [14]. Copyright 2018, American Chemical Society. (d) The STEM-HAADF image of a cross-sectional Pero-LEDs based on the ultra-thin perovskite of $\text{PBABr}_y(\text{Cs}_{0.7}\text{FA}_{0.3}\text{PbBr}_3)$. (e) The corresponding EQE and (f) EL spectra with the operation voltage increasing. Reproduced with permission from Ref. [17]. Copyright 2019, Springer Nature.

452, 452, and 505 nm corresponding to $n = 1, 2, 3$, and 4 of the quasi-2D perovskite of $\text{PA}_2(\text{CsPbBr}_3)_{n-1}\text{PbBr}_4$ (here, PA is propylammonium) were existing, and the main emission peak of 505 nm was due to the charge-transfer. After optimization, a cyan Pero-LED emitting at 505 nm (Fig. 2(e)) and with an EQE_{max} of 3.6% was obtained. To control the formation of quasi-2D perovskites with a desired n values, Xing *et al.*[30] demonstrated a strategy replacing the long ligands (PEA) with shorter ones (iso-propylammonium, IPA) to reduce van der Waals interactions, which successfully slowed the formation of $n = 1$ phase and improved the monodispersity of $n = 2, 3, 4$ phases. With this strategy, the as-synthesized quasi-2D perovskite films exhibit a single emission peak and color-stable blue emission at 477 nm. Moreover, the as-fabricated sky-blue Pero-LEDs (emission at 490 nm, Fig. 2(f)) obtained a maximum luminance (Lv_{max}) of 2480 cd/m^2 and EQE_{max} of 1.5%. To further stabilize the quasi-2D perovskite crystals and block the carrier diffusion in a bias condition, Shang *et al.*[31] introduced the inorganic crystalline Cs_4PbBr_6 to homo-

geneously surround the quasi-2D perovskite (Fig. 2(g)). The Pero-LEDs based on such a structure achieved a Lv_{max} of 3259 cd/m^2 and an EQE_{max} of 4.51% with emission at 500 nm. Besides, the performance of the operational stability of devices was enhanced dramatically. As shown in Fig. 2(h), the lifetime was increased to more than 1 h, and the EL spectra curves of 0 and 12 h are almost completely unchanged.

Although some progress has been made in phases stability and performance enhancement of Pero-LEDs based on quasi-2D perovskites, the efficient pure and deep blue-emitting devices are still difficult to fabricate owing to the poor electrical conductivity caused by the excess organic ligands adding. To overcome this obstacle, the as-synthesized QDs, NPs and ultra-thin quasi-2D perovskites are reported. With these strategies, the size of the perovskite emitting units could also be reduced to the nanoscale, and the bandgap will be enlarged due to the quantum confined effect. In 2015, Song *et al.*[11] firstly reported the Pero-LEDs based on all-inorganic QDs of CsPbBr_3 , and the emission peaks were success-

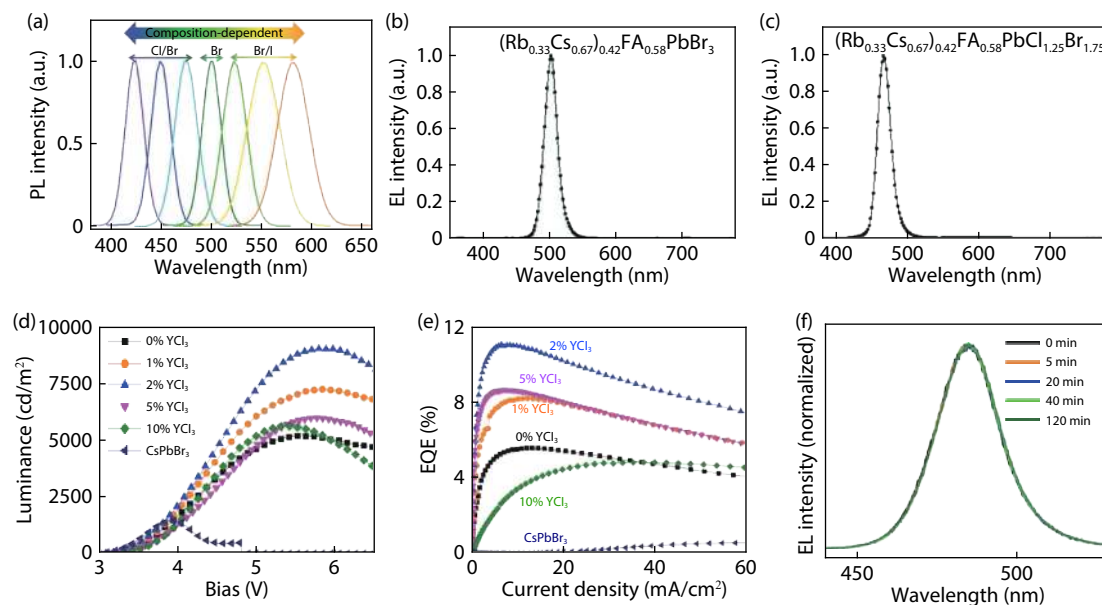


Fig. 4. (Color online) Blue-emitting perovskites prepared by applying several methods simultaneously. (a) Composition-tunable PL spectra of perovskite CsPbX_3 QDs by adding the different halides. Reproduced with permission from Ref. [13]. Copyright 2015, WILEY-VCH. The EL spectra of Pero-LEDs based on the perovskites of (b) $(\text{Rb}_{0.33}\text{Cs}_{0.67})_{0.42}\text{FA}_{0.58}\text{PbBr}_3$ and (c) $(\text{Rb}_{0.33}\text{Cs}_{0.67})_{0.42}\text{FA}_{0.58}\text{PbBr}_{1.75}\text{Cl}_{1.25}$. Reproduced with permission from Ref. [33]. Copyright 2019, The Royal Society of Chemistry. (d) The luminance-bias and (e) EQE-current density curves of CsPbBr_3 : PEACl (1 : 1) devices with different ratios of YCl_3 . And (f) the EL spectrum stability test of a Pero-LED based on CsPbBr_3 : PEACl : 2% YCl_3 with continuous bias of 3.2 V for 120 min. Reproduced with permission from Ref. [9]. Copyright 2019 Springer Nature.

fully shifted from 470 to 515 nm by controlling the size of QDs (Fig. 3(a)). The particle size control around from 2 to 8 nm was realized by changing the reaction temperature, the reaction temperature was 140, 155, 170, and 185 °C, respectively. Besides, the NPs of CsPbBr_3 was reported by Yang *et al.*[32] and Bohn *et al.*[14], and the emission covered the range of 442–459 nm (Fig. 3(b)) and 432–520 nm (Fig. 3(c)) respectively. Moreover, deep blue-emitting Pero-LEDs based on CsPbBr_3 NPs were fabricated and obtained an EQE_{max} of 0.057% with emission at 464 nm. Recently, an ultra-thin quasi-2D perovskite was reported by Liu *et al.*[17], the thickness was reduced to ~ 9 nm (as shown in the cross-sectional STEM-HAADF image, Fig. 3(d)). The corresponding Pero-LEDs achieved an EQE_{max} of 9.5% (Fig. 3(e)) at a luminance of 54 cd/m^2 with emission at 483 nm (Fig. 3(f)). This impressive growth of EQE was achieved mainly by the reduction of the insulating organic ligands, and the blue-shift emission was due to the effective quantum-confined effects caused by the ultra-thin thickness and quasi-2D structure of perovskite.

However, there are still many problems for QDs, NPs, and ultra-thin quasi-2D perovskites, such as current leakage caused by the low coverage of the emitting layer. To fabricate efficient and color stable blue-emitting Pero-LEDs, we should combine the several methods of preparing blue-emitting perovskites. Firstly, the halogen doped method could be used in the synthesis of QDs and NPs to improve the ability of bandgap adjustment. Song *et al.*[13] demonstrated that the CsPbBr_3 QDs could obtain an emission from 470 to 515 nm by controlling the size of QDs, while the $\text{CsPb}(\text{Br}_x\text{Cl}_{1-x})_3$ QDs could emission from 420 to 515 nm (Fig. 4(a)). And A-site doping in the synthesis of QDs was reported by Meng *et al.*[33], the Pero-LEDs based on $(\text{Rb}_{0.33}\text{Cs}_{0.67})_{0.42}\text{FA}_{0.58}\text{PbBr}_3$ achieved a Lv_{max} of ~ 1000 cd/m^2 and an EQE_{max} of 3.6% with emission at 502 nm (Fig. 4(b)). And a deep blue-emitting Pero-LED

(emission at 466 nm, Fig. 4(c)) based on $(\text{Rb}_{0.33}\text{Cs}_{0.67})_{0.42}\text{FA}_{0.58}\text{PbBr}_{1.75}\text{Cl}_{1.25}$ was also fabricated, and an EQE_{max} of 0.61% was obtained. Recently, Wang *et al.*[9] reported a blue-emitting Pero-LED (emission at 485 nm) with a recorded Lv_{max} of 9040 cd/m^2 (Fig. 4(d)) and a recorded EQE_{max} of 11% (Fig. 4(e)), which based on the perovskite of CsPbBr_3 :PEACl: 2% YCl_3 prepared by halide mixing and B-site doping in the quasi-2D perovskite. Besides, an impressive excellent EL spectrum stability was also obtained. As shown in Fig. 4(f), there was almost no shift of EL peaks with a continuous bias of 3.2 V for 120 min.

The summaries in Table 1 show that researchers have started to combine the strategies of compositional engineering and size controlling of emitting units. Pero-LEDs with high EQEs were fabricated based on the perovskites prepared by the comprehensive strategies. However, we believe that a more effective combination of the strategies could be carried out to fabricate the blue-emitting Pero-LEDs with spectrally stable emission and high EQE.

3. Challenges and future outlook

Although great progress has been achieved in the blue-emitting Pero-LEDs fabrication in the past few years, the high-efficiency deep-blue-emitting (440–470 nm) devices are still lacking in demonstrations. We list and draw an EQE evolution curve in Fig. 5 using the reported EQEs of blue-emitting Pero-LEDs, most EQEs of Pero-LEDs with the emission peak at less than 480 nm are no more than 3%, and that ones with the emission peak at less than 440 nm are no more than 1%. Besides, improving the EL spectra stability and operational stability of the blue-emitting Pero-LEDs are still big challenges. To overcome these obstacles, we need to utilize the two strategies (compositional engineering and size controlling of the emitting units) comprehensively and optimize the device

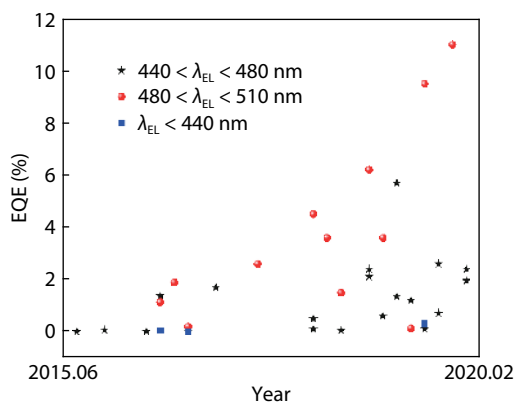


Fig. 5. (Color online) The recorded EQEs of blue-emitting Pero-LEDs in recent years.

structure of Pero-LEDs.

3.1. Developing spectrally stable deep-blue emission

Considering the side effects of using a single method to tune the emission of Pero-LEDs to deep-blue gamut, the strategies using several methods simultaneously were studied. Shang *et al.*^[31] and Zou *et al.*^[34] reported a similar strategy using the inorganic large bandgap Cs_4PbBr_6 to surrounding the quasi-2D perovskites. With this strategy, they successfully obtained the spectrally stable emission of Pero-LEDs. However, the emission colors are not blue enough, which are 500 and 484 nm respectively. If more methods such as halogen-doped and A-site doped are applied, the spectra stable emission may obtain a blue-shift. Tan *et al.*^[35] demonstrated a stable ultra-pure blue (468 nm) emitting of Pero-LEDs based on the perovskite of 2-phenoxyethylamine-passivated $\text{CsPbBr}_x\text{Cl}_{3-x}$, and a square-wave alternating voltage was applied at the same time. And some ions doping such as potassium ion (K^+), Rb^+ , manganese ion (Mn^{2+}), and nickel ion (Ni^{2+}) could effectively passivate the perovskite crystals and stable the emission spectra of Pero-LEDs.

3.2. Improving efficiency and operation stability

To fabricate the high-efficiency and operational stable blue-emitting Pero-LEDs, only improving the performances of perovskites is not enough. It is also critical to improve the charge injection ability and control the injection balance of electrons and holes by optimizing the structure of Pero-LEDs. Gangishetty *et al.*^[22] demonstrated a transport layer structure using poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(4,4'-(N-(4-sec-butylphenyl) diphenylamine))] (TFB) and Nafion perfluorinated ionomer (PFI) as hole transport layer instead of traditional NiO_x to maintain robust nanocrystal emission, and an enhanced EQE_{max} of 0.5% with emission at 469 nm was achieved. Ren *et al.*^[36] demonstrated an efficient hole transport bi-layer structure composed of poly(sodium-4-styrene sulfonate) (PSSNa) and NiO_x , which could simultaneously inhibit the nonradiative decays between NiO_x and perovskite films by reducing NiO_x surface defects and improve quasi-2D perovskite thin film quality by minimizing its pin-holes and reducing the film roughness. With this architecture, an EQE_{max} of 1.45% and a remarkable luminance of 4359 cd/m^2 were obtained.

4. Conclusion

We have summarized the strategies of preparing blue-

emitting perovskites and discussed their advantages and disadvantages. The compositional engineering strategies could precisely adjust the bandgap of perovskites. However, the drawbacks (e.g., phase segregation and poor quality of film morphology) could not be ignored. More environmentally stable blue-emitting perovskites could be obtained by size controlling of perovskite crystals. However, the size is hard to be controlled precisely and tending to be inhomogeneous. Hence, the strategies should be utilized comprehensively to improve the performances of blue-emitting perovskites. Moreover, we also discussed the challenges of fabricating high-efficiency stable blue-emitting Pero-LEDs. The most urgent challenge is increasing the EQE and keeping the deep blue emission at the same time. Researchers should then pay more attention to the spectral stability and the long operational lifetime of blue-emitting Pero-LEDs. We believe that the high-efficiency stable blue-emitting Pero-LEDs will be fabricated by improving the performances of perovskites and optimizing the architecture of Pero-LEDs.

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