RESEARCH HIGHLIGHTS

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# Star perovskite materials

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Nowadays, perovskite materials become research hotspots with the soar of the power conversion efficiency (PCE) for perovskite solar cells. Specifically, metal halide perovskites (MHPs), with the formula $ABX_3$ (A = $CH_3NH_3^+$ ($MA^+$), $CH(NH_2)_2^+$ ($FA^+$), $Cs^+$, etc.; B = $Pb^{2+}$ or $Sn^{2+}$; and X = $I^-$, $Cl^-$ and/or $Br^-$), have become star materials in optoelectronics. MHPs present favorable optoelectronic properties, like high absorption coefficient in visible range, long carrier diffusion length, high defect tolerance, and superior optical gain in a wide wavelength range. These merits gift MHPs promising potential in optoelectronic application, including solar cells, light-emitting diodes, photodetectors and lasers. This article introduces the star perovskite materials in milestone works and highlights the best-performing materials in respective optoelectronic application.

Perovskite solar cells (PSCs) occupy a predominant position in the new-generation photovoltaics due to the skyrocketing PCE from 3.8% to 25.5% during last 12 years[1, 2]. They can be divided into organic–inorganic hybrid cells and all-inorganic cells according to cations in the A position. $MAPbX_3$ (X = I/Br) as a visible-light sensitizer was first reported with an efficiency of 3.8% in 2009[1]. Subsequently, $FA^+$ was found to be a superior candidate for A-site cation, which extends optical absorption and allows higher theoretical efficiency. However, because of the larger size of $FA^+$, pure $FAPbI_3$ suffers from phase instability at room temperature, since it can crystalize into two phases: photoinactive $\delta$-phase (yellow phase) and photoactive $\alpha$-phase (black phase). Mixing cations and halide ions (e.g., $MA^+$, $Cs^+$ or $Br^-$) were common approaches to stabilize the $\alpha$-phase. Seo *et al.*[3] used a small amount of $MAPbBr_3$ to stabilize $FAPbI_3$, and the resulted PSCs gave a PCE of 25.6% (certified 25.2%). Recently, Seok *et al.*[2] improved the efficiency of $FAPbI_3$ solar cells to 25.8% (certified 25.5%) by interface modification, which is the highest record for PSCs by far (Figs. 1(a) and 1(b)). A $FASnCl_x$ interlayer formed between Cl-bonded $SnO_2$ and $MDACl_2$-containing $FAPbI_3$ film, passivating the buried interface and enabling efficient charge transport and extraction. $CsPbI_xBr_{3-x}$ solar cells exhibit potential in photovoltaics due to good thermal stability and suitable bandgap for the top cell of tandem devices. However, the nonradiative charge recombination caused by the defects in perovskites results in photovoltage loss, limiting the PCE. Liu *et al.*[4] used histamine (HA) to passivate the surface defects of $CsPbI_{3-x}Br_x$ film. The amount of uncoordinated $Pb^{2+}$ on surface was decreased and the carrier lifetime was extended, yielding a PCE of 20.8%, which is the highest record to date for all-inorganic PSCs. Moreover, the lead toxicity motivated the exploration on less-lead and lead-free PSCs. Sn can partly or totally replace Pb in perovskites due to their similar electronic structures. In fact, the introduction of Sn can reduce the bandgap to 1.3–1.4 eV, which lifts the theoretical PCE. Besides, it can be used in low-bandgap bottom cell in tandem devices. However, $Sn^{2+}$ is chemically unstable and can be easily oxidized to $Sn^{4+}$ in air, making it challenging to fabricate pure Sn-based perovskites. The PCE of $FA_{0.5}MA_{0.45}EA_{0.05}Sn_{0.5}Pb_{0.5}I_3$ PSCs reached 22.02%[5]. A reducing agent 4-hydrazinobenzoic acid (HBA) together with $SnF_2$ was used to restrain $Sn^{2+}$ oxidation. He *et al.*[6] introduced FPEABr into $FASnI_3$ precursor solution to form a 2D/3D structure. With 10% FPEABr, the PCE was increased to 14.81% (certified 14.03%), which is the highest value for Sn-based PSCs to date. Fig. 1(c) presents the record efficiencies for different PSCs.

Perovskite light-emitting diodes (PeLEDs) are competitors to organic LEDs and traditional LEDs because of the adjustable bandgap, high photoluminescence quantum yields (PLQYs) and narrow PL emission spectra, which enables high brightness and color purity. However, the low exciton binding energy in perovskites causes dominating nonradiative recombination over radiative recombination. Extensive strategies, including depositing ultra-thin emission layers, featuring nanoscale polycrystalline grains, synthesizing 0D colloidal nanocrystals (NCs) or quantum dots (QDs), and fabricating 2D or quasi-2D perovskites, could effectively increase exciton binding energy and enhance PLQY through quantum confinement effect. The emission color of perovskites can be tailored mainly through two strategies: one is tuning the composition of A-site cations and X-site halide anions, thus the emission from whole visible range can be achieved[7] (Fig. 1(d)); the other is manipulating dimension by organic spacers or ligands in low-dimensional systems. The electroluminescence phenomenon of perovskites could date back to 1992, but it did not attract much attention due to the low external quantum efficiencies (EQEs) until Friend *et al.* reported $MAPbX_3$ LEDs (EQE < 1%) in 2014[8]. From then on, PeLEDs advanced with huge breakthroughs. The EQE for near-infrared (NIR), red, and green LEDs have exceeded 20%[9–12] (Fig. 1(e)). For NIR PeLEDs (780–1000 nm), most of the high EQEs (>20%) were obtained from $FAPbI_3$ with either 3D or quasi-

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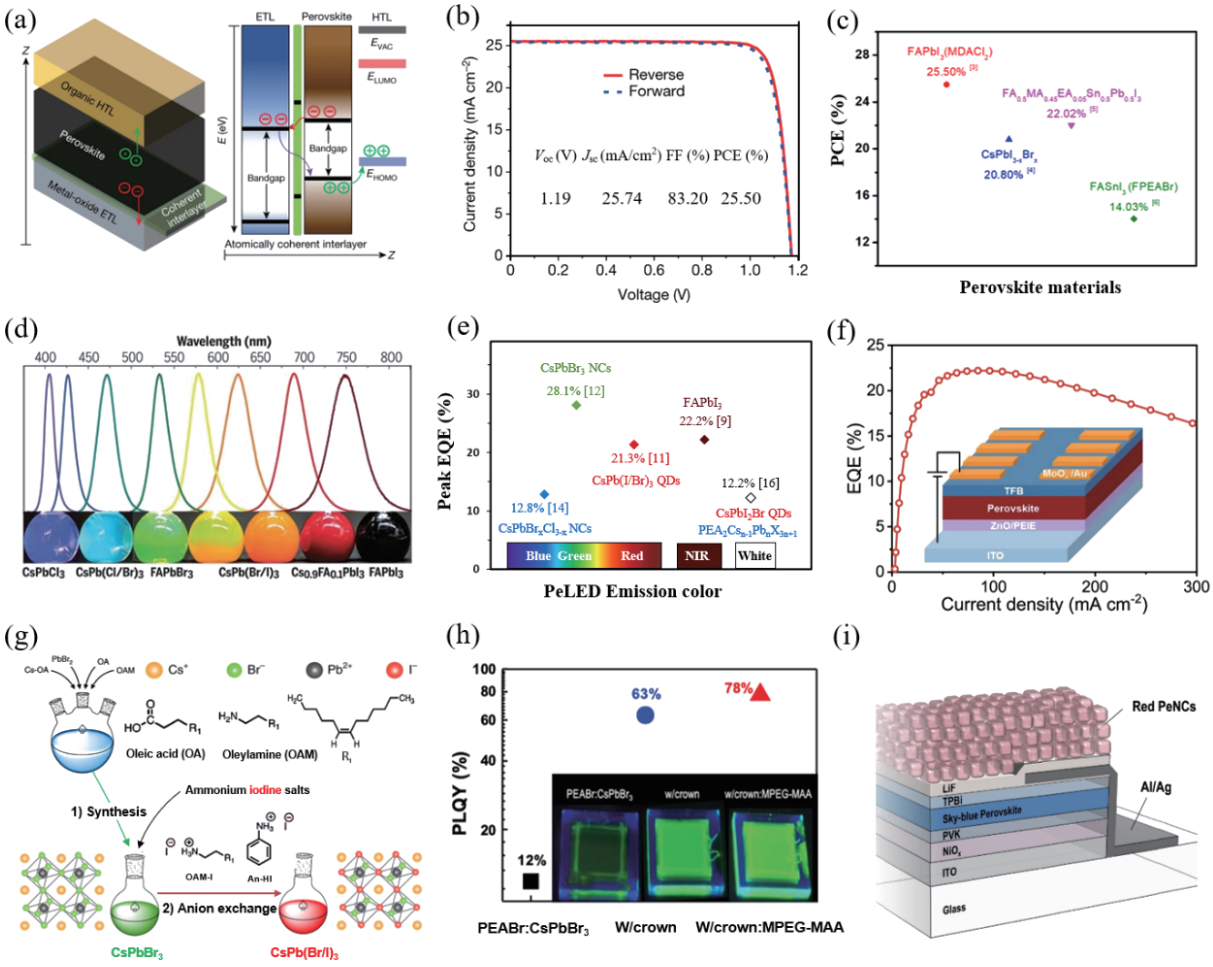


Fig. 1. (Color online) (a) Left, the PSC with the highest certified PCE. Right, the energy diagram. (b) *J*–*V* curves. Reproduced with permission[3], Copyright 2021, Springer Nature. (c) The highest PCE values and the corresponding materials. (d) The PL spectra for colloidal perovskite NCs. Reproduced with permission[7], Copyright 2017, Science (AAAS). (e) The highest EQEs so far for blue, green, red, NIR and white PeLEDs, respectively. (f) EQE *vs* current density curve for the best NIR device. Reproduced with permission[9], Copyright 2021, Springer Nature. (g) The synthesis of red-emissive $CsPb(Br/I)_3$ QDs through anion-exchange from pristine $CsPbBr_3$ QDs. Reproduced with permission[11], Copyright 2018, Springer Nature. (h) PLQYs of quasi-2D PEABr:$CsPbBr_3$ films without or with crown and crown:MPEG-MAA additives. Reproduced with permission[12], Copyright 2021, Wiley-VCH. (i) The structure of the most efficient white PeLED. The red perovskite NCs were deposited on top of a sky-blue PeLED. Reproduced with permission[16], Copyright 2021, Elsevier.

2D structures[9, 10]. Wang *et al.* utilized 2-(2-(2-aminoethoxy)ethoxy)acetic acid (AEAA) as an additive to assist vertically-orientated growth of $FAPbI_3$ crystallites[9]. The resulted device emitted ~800 nm light and presented a 22.2% peak EQE (Fig. 1(f)), which is currently the highest record for NIR PeLEDs. To achieve pure red (620–650 nm) PeLEDs, mixed halide perovskites are adopted, but they suffer from spectral instability caused by phase segregation. $CsPb(I/Br)_3$ QDs, synthesized through anion exchange by adding alkyl ammonium iodine salt into $CsPbBr_3$ QD solution, gave an impressive EQE of 21.3%[11] (Fig. 1(g)). The QD film gave a deep red emission at 649 nm with high color purity. As for green PeLEDs (510–550 nm), Hou *et al.* recently reported highly efficient green LEDs based on PEABr:$CsPbBr_3$ NCs with quasi-core/shell structure[12]. The peak EQE reached 28.1% at 525 nm, which stands for the highest record for all PeLEDs so far. In this work, 18-crown-6 (crown) and poly(ethylene glycol)methyl ether acrylate were used to inhibit the self-aggregation of PEABr and transform the structure from quasi-2D to NCs. The dual-additive-treated perovskite presented low defect density, as evidenced by the great enhancement of PLQY from 12% to 78% (Fig. 1(h)). Although the EQE of green and red PeLEDs exceeds 20%, the efficiency of blue PeLEDs (450–486 nm) lags far behind[13]. The most efficient blue LED by far was made from $CsPbBr_xCl_{3-x}$ NCs (emitted at 486 nm), with a maximum EQE of 12.8%[14]. Tang *et al.* utilized ethanolamine (ETA)-modified PEDOT:PSS to induce dense heterogeneous nucleation at the interface and inhibit large grain growth. Small crystallites with reduced defect density were obtained, which favored the radiative recombination. Owing to the poor efficiency of blue PeLEDs and the spectral instability of pure red PeLEDs, making highly efficient white PeLEDs is still challenging[15]. Recently, a white PeLED with an EQE of >12% was realized through near-field optical coupling between a sky-blue LED and red perovskite NCs (Fig. 1(i))[16]. The sky-blue PeLED made from quasi-2D $PEA_2Cs_{n-1}Pb_nX_{3n+1}$ emitted at 493 nm while the red perovskite NCs of $CsPbI_2Br$ emitted at 650 nm. The ultra-thin interlayer allowed energy transfer from sky-blue LED to the red-emission region, where red-emissive NCs converted it into red light, further mixing with blue light to

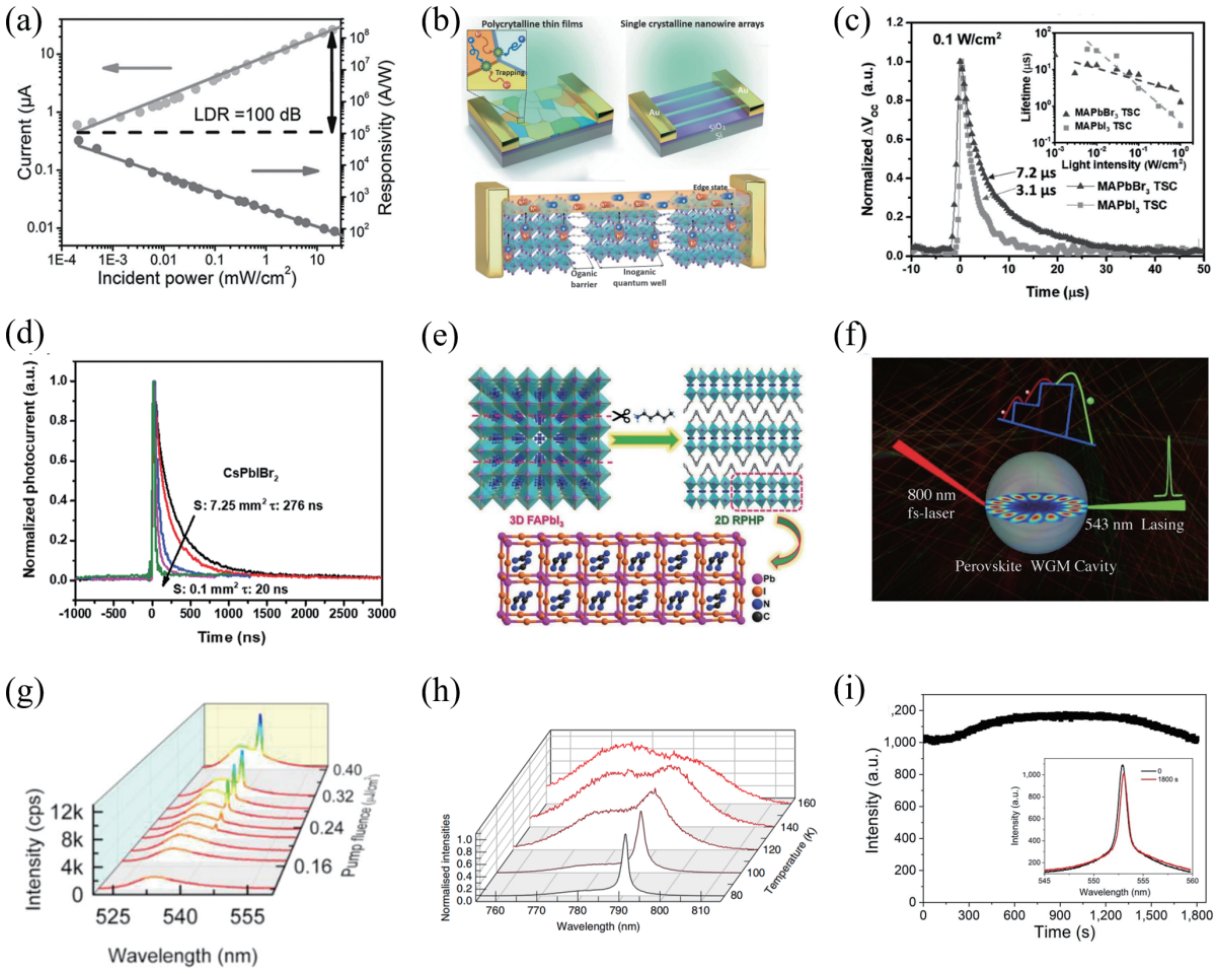


Fig. 2. (Color online) (a) Power-dependent photocurrent and responsivity for $CsPbBr_3$ microcrystal photodetector (3 V bias). Reproduced with permission[17], Copyright 2017, Wiley-VCH. (b) The photodetector based on polycrystalline thin films and single-crystalline nanowire arrays of 2D perovskite; the schematic of carrier dynamics in the photodetector. Reproduced with permission[18], Copyright 2018, Springer Nature. (c) Transient photovoltage of photodetectors based on $MAPbBr_3$ TSCs under green light illumination of 0.1 W/cm². Reproduced with permission[19], Copyright 2017, Wiley-VCH. (d) Transient photocurrent curves for $CsPbIBr_2$ photodetectors with different active areas. Reproduced with permission[20], Copyright 2018, Wiley-VCH. (e) Tailoring a 3D prototype of $FAPbI_3$ into 2D Ruddlesden-Popper structure. Reproduced with permission[21], Copyright 2019, Wiley-VCH. (f) Upconverted single-mode lasing from an individual $CsPbBr_3$ microsphere with an ultrahigh quality-factor. Reproduced with permission[22], Copyright 2018, Wiley-VCH. (g) Single-mode lasing spectra of a $CsPbBr_3$ submicron plate at different pump fluence. Reproduced with permission[23], Copyright 2021, Wiley-VCH. (h) Amplified spontaneous emission spectra under CW excitation at various temperatures and constant pump intensity. Reproduced with permission[24], Copyright 2019, Springer Nature. (i) Operational stability of quasi-2D based laser under CW excitation with an intensity of 2 kW/cm². Inset: lasing spectra before (black) and after (red) continuous pumping. Reproduced with permission[25], Copyright 2020, Springer Nature.

emit white light. A luminance of 2000 cd/m² was achieved.

The performance parameters for perovskite photodetectors (PPDs) include responsivity ($R$), detectivity ($D^*$), linear dynamic range (LDR) and response time. Responsivity describes the photoelectric conversion ability of PPDs. Yang *et al.*[17] prepared $CsPbBr_3$ microcrystal films by solution growth method. The PPDs had an ultrahigh $R$ of $6 \times 10^4$ A/W, which is one order of magnitude higher than the previously reported counterparts (Fig. 2(a)). Detectivity reflects the sensitivity of a PD to weak light. The noise current of the device directly affects the detectivity of PDDs. In 2018, Feng *et al.*[18] designed nanowire arrays based on 2D perovskite $(BA)_2(MA)_{n-1}Pb_nI_{3n+1}$ ($n$ = 2–5) to inhibit noise current. The direction of nanowire arrays was perpendicular to that of 2D perovskite layers (Fig. 2(b)). The organic barrier in 2D perovskite could suppress charge transport along nanowire interior, thus decreasing dark current. The noise current was effectively reduced, yielding a high detectivity of over $7 \times 10^{15}$ Jones (irradiance $10^{-6}$ mW/cm²). LDR refers to the stable response range of PPDs under light illumination. In 2017, a $MAPbBr_3$ thin-single-crystal (TSC) PD was reported by Huang *et al.*[19] It showed linear response to green light from 0.35 pW/cm² to 2.1 W/cm², corresponding to a LDR of 256 dB. The absence of grain boundaries could reduce charge recombination and enable a linear response under strong light. The carrier lifetime for $MAPbBr_3$ TSC PD under 1 W/cm² light is larger than 1 μs, longer than the charge extraction time (~100 ns) (Fig. 2(c)). The $MAPbBr_3$ PD could keep linear response to light intensity higher than 1 W/cm². Response speed reflects the sensitivity of PDs to dynamic optical signal. In 2018, Gao *et al.*[20] made a $CsPbIBr_2$-based self-driven PD with a response time of 20 ns, which is among the best performances

for 3D PPDs (Fig. 2(d)). Han *et al.*[21] synthesized a 2D Ruddlesden-Popper perovskite $(PA)_2(FA)Pb_2I_7$ in 2019, consisting of corner-sharing $PbI_6$ octahedra (Fig. 2(e)). The PD exhibited a response time of ~2.54 ns, which is the record for 2D PPDs.

A laser is a strong coherent light source consisting of a gain medium, a pump source, and an optical cavity. The gain medium is a material capable of amplifying light through stimulated emission. As an excellent optical gain medium, perovskite materials have been successfully applied in lasers due to their low threshold, high coherence, and high quality-factor. In 2018, Tang *et al.*[22] prepared $CsPbBr_3$ spheres (~780 nm), which could be used not only as optical gain medium, but also as whispering-gallery cavity (Fig. 2(f)). The laser had an ultrahigh quality-factor of ~$1.5 \times 10^4$, which is the best among reported results. Lan *et al.* reported $CsPbBr_3$ submicron plates-based single-mode lasing with a threshold of ~0.22 $\mu J/cm^2$ (Fig. 2(g)), which is the lowest among perovskite lasing since it was reported[23]. Making continuous wave (CW) operation at room temperature has been a major challenge for 3D perovskite lasers due to the phase instability of the crystal lattice at room temperature, the limited thermal conductivity and screening effects[24]. In 2019, Brenner *et al.* first reported a CW lasing with $Cs_{0.1}(MA_{0.17}FA_{0.83})_{0.9}Pb_{0.84}(I_{0.84}Br_{0.16})_{2.68}$ as the gain medium. This mixed-cation perovskite presented CW optical gain at 80–120 K (Fig. 2(h)), which is currently the widest temperature range for 3D CW lasing. Qin *et al.*[25] reported a stable quasi-2D perovskite $(NMA/PEA)_2FA_{n-1}Pb_nBr_{3n+1}$. Its laser could work under CW optical pumping in air at room temperature. The intensity kept unchanged after 1800 s CW excitation with an intensity of 2 $kW/cm^2$ (in air, RH 55%), and the lasing spectrum maintained its peak without shifting (Fig. 2(i)). This is the most stable perovskite-based CW mode laser reported so far.

In conclusion, apart from the great breakthrough in PSCs, perovskites exhibit good performance in other optoelectronic devices like LEDs, PDs, and lasers. Those star materials are overviewed here. The challenges on environmental stability, scaling up and lead toxicity still remain. More efforts are needed to develop new materials and to improve the device performance.

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