• MINI REVIEWS •

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Organolead trihalide perovskite materials for efficient light emitting diodes

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Organolead trihalide perovskite materials have been attracting increasing attention due to their promising role in solid solar cells. Several advantages make them potential candidates for optoelectronics: (1) solution- or/and vapor-processed preparation at low temperature; (2) tunable optical bandgap, wide absorption spectrum but narrow photoluminescence peaks; (3) long carrier life time, large diffusion length and high charge mobility; (4) various nanostructures via tuning capping agents and solvents. In this review, we summarize recent attempts toward efficient LEDs based on organolead trihalide perovskite materials. The strategies of materials science, device design and interface engineering are highlighted. Recent development and future perspectives are summarized for practical perovskite light technologies.

organolead trihalide, perovskite materials, interface engineering, light emitting diodes

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1 Introduction

Light emitting diodes (LEDs) are the potential energysaving candidate for the next generation of illumination and displays. Compared with traditional light sources (e.g. incandescent lamp, fluorescent lamp), LEDs have several advantages, including: (1) high brightness but low radiation heat; (2) high energy efficiency but low working voltage; (3) tunable visible spectrum and negligible ultraviolet exposure; (4) high reliability and long lifetime; (5) easy preparation and acceptable performance/cost ratio, which have attracted both academic and industrial attention. Upon application of a suitable voltage to the device, electrons and holes were injected to the p-n junction and combined in the emitting layer to release energy by photon radiation. For efficient electroluminescence, novel materials, interface engineering, structure design and device physics were involved in the LEDs researches. Various light emitters, including crystal inorganic semiconductors of III–V group [1,2] and IV group [3,4], II–VI group quantum dots [5,6], organic/organometallic/polymer materials [7–9], and carbon nanomaterials [10,11], have been applied to LEDs and contributed to efficient devices. Though recent studies have made many improvements for scientific research and industrial production, inexpensive, solution processable, scalable and efficient functional materials are under exploration for future LEDs applications.

Nowadays, there is an increasing interest in inorganicorganic organolead trihalides (RNH₃PbX₃, R=alkyl group,

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X=Cl, Br, I). In the structure (Figure 1), they own Pb ion in the cubic center, RNH3 at each vertex of the cubic and X at each face center of the cubic; or corner-sharing PbX₆ octahedras and small-sized RNH₃ in the voids between the octahedras [12,13]. With RNH₃ cations of suitable size, the ordered arrangement expands and three-dimensional (3D) crystals could be achieved. Due to the combination of inorganic and organic part in the molecule scale, this class of hybrid materials shares the properties of both kinds, such as good charge transport and narrow bandgap like inorganic species, high absorption coefficient and good solubility like organic species. Several advantages make them potential candidates for optoelectronics: (1) they can be solutionor/and vapor-processed at low temperature (typically< 150 °C), resulting in crystalline thin film in an energy saving way; (2) they have tunable optical bandgap covering the visible and infrared regions via component adjustment, along with wide absorption spectrum but narrow photoluminescence peaks; (3) they have long carrier life time, large diffusion length and high charge mobility for balanced electrons and hole transportation; (4) they have various nanostructures by simply tuning capping agents and solvents, which could make them promising candidates for nanoscale applications.

Among the inorganic-organic organolead trihalides, CH₃NH₃⁺ based hybrid perovskite materials have attracted most attention from photovoltaics. In the early report, CH₃NH₃PbI₃ and CH₃NH₃PbBr₃ were used as a sensitizer for liquid dye-sensitized solar cells yielding efficiency of 3.8% [14]. In 2012, Snaith et al. [15] and Grätzel et al. [16] reported CH₃NH₃PbI_{3-x}Cl_x and CH₃NH₃PbI₃ thin film for solid solar cells with Spiro-OMeTAD as the hole transport layer at almost the same time, which opened a door toward novel solid photovoltaics. And recent perovskite solar cells based on NH=CHNH₃PbI₃ have achieved certified efficiency of 20.1% [17], comparable efficiency with that of silicon solar cells. The success in photovotaic cells extended the knowledge of inorganic-organic hybrid perovskite materials [18-22] and inspired their research for other optoelectronics, such as light emitting diodes [23-25], lasers [26-29], and photodetectors [30-33]. In 2014, Friend and co-workers [25] reported high-brightness infrared and visible light emitting diodes (PeLEDs) based on perovskite materials.



Figure 1 (a) Model of the basic perovskite structure; (b) the extended network structure connected by the corner-shared octahedra. A represents RNH₃⁺, M represents the central metal ion, and X represents halogen ion [12] (color online).

Since then, this very field has been attracting increasing attention.

Recently, though some reviews have highlighted the success of PeLEDs [22–24], there is no systemic review about materials science and interface engineering for the cutting-edge studies. In this review, we summarize recent attempts toward efficient LEDs based on organolead trihalide perovskite materials. The strategies of materials science, device design and interface engineering are highlighted. Recent development and future perspectives are summarized for practical perovskite light technologies.

2 Organolead trihalide thin films for efficient LEDs

Organolead trihalide perovskite thin film was prepared through one-step process in the early trials. The precursor solution containing stoichiometric molar ratio of PbX₂ and RNH₃X (R=alkyl group, X=halogen) in polar solvent, such as γ -butyrolactone, N,N-dimethylformamide (DMF) and dimethyl sulphoxide (DMSO), was spin-coated on substrates and thermal annealed for about an hour at ~100 °C for film crystallization [14–16,34]. Due to the convenience of operation, this approach is employed for PeLEDs in most recent reports. With gaseous reactions, PbX₂ and RNH₃X vapor deposition could directly form uniform polycrystalline perovskite thin film [35]. Sequential deposition during which PbX₂ reacted with RNH₃X solution or vapor could also contribute to smooth functional thin film [17,36,37]. These modified preparation methods have achieved improved device performance in perovskite solar cells, and would be promising alternatives for PeLEDs.

The initial idea of applying organolead trihalide perovskite materials for LEDs was reported at the end of the 20th century. Two-dimensional perovskite materials $((R-NH_3)_2$ -PbX₄, R=alkyl group, X=halogen) were involved as emitter in the solid electroluminescence device. The devices exhibited narrow emitting peak, but they could only work under high voltage (>20 V), inert environment and low temperature (e.g. liquid nitrogen temperature) [38–43]. This area did not attract wide attention probably due to the poor device performance compared with well-developed LED types. Opportunities might be created in new generation of perovskite materials.

In 2014, Friend and co-workers [25] reported highbrightness infrared and visible PeLEDs, which could operate at room temperature. In the infrared PeLEDs, CH_3NH_3 -PbI_{3-x}Cl_x was located between large-bandgap semiconductors TiO₂ and F8 to confine injected charges for efficient recombination (Figure 2(a)). The near-infrared electroluminescence was centered at 754 nm with the full-width at halfmaximum (FWHM) of 35 nm (Figure 2(a)). The turn-on voltage was only 1.5 V and external quantum efficiency (EQE) reached 0.23% at 5.3 V. Modifiying the TiO₂/perovskite interface with Al₂O₃ thin layer, the device achieved radiance of 13.2 W sr⁻¹ m⁻² with EQE of 0.76%. The PeLEDs (ITO/PEDOT:PSS/perovskite/F8/Ca/Ag) based on CH₃NH₃PbBr₃ and CH₃NH₃PbBr₂I emitters achieved bright green electroluminescence at 517 nm and red electroluminescence at 630 nm, respectively. And the former achieved a luminance of 364 cd m⁻² at a current density of 123 mA cm⁻² with EQE of 0.1%. The versatility of these organolead trihalide perovskite materials could reasonably contribute to multi-colored lighting and display. This work extended the material horizons of LEDs and laid the foundation for further explorations, covering interface engineering, preparation process, device physics, flexible applications, etc.

Due to the disadvantages of instability, low transport rate and high cost, replacing the organic and polymer hole transport or electronic block materials could push forward the commercial PeLEDs. Hoye *et al.* [44] prepared bright PeLEDs with structure of ITO/PEDOT:PSS/ CH₃NH₃PbBr₃/ ZnO/Ca/Ag, achieving maximum luminance of 550 cd m⁻². In the process of spatial atmospheric atomic layer deposition (SAALD), doping ZnO with 40% Mg²⁺ resulted in barrier-less electron injection (Figure 3) and could reduce the turn-on voltage by ~1 V. Compared with F8 based PeLEDs that suffer from oxidation defects, this device exhibited lower FWHM of 25 nm and more stable electroluminescence spectra, which paves the way toward high definition display. However, the reliability of device fabrication should be further improved.



Figure 2 (a) Energy-level diagram of $CH_3NH_3PbI_{3-x}Cl_x$ based infrared PeLEDs; (b) absorption and normalized emission spectra of $CH_3NH_3PbI_{3-x}Cl_x$ perovskite. Electroluminescence (green line) occurs at 754 nm and photoluminescence (red line) at 773 nm [25] (color online).

To overcome the electron-injection barrier in PeLEDs and improve surface coverage of perovskite films, Wang *et al.* [45] reported polyethyleneimine (PEI) interlayer for PeLEDs (ITO/PEI-ZnO/perovskite/TFB/MoO_x/Au). The hydrophilic interlayer allows high-quality perovskite thin films and provides low work-function interface for electron injection. CH₃NH₃PbI_{3-x}Cl_x based LED turns on at 1.3 V, the best EQE reaches 3.5% at 2.2 V (160 mA cm⁻²), respectively. The green device based on CH₃NH₃PbBr₃ achieved maximum luminance of 20 000 cd m⁻² with power efficiency of 4.0 lm W⁻¹ and EQE of 0.8% at 2.8 V. This work indicates that interface engineering acts as an important progress toward low-cost, efficient and bright PeLEDs.

Of equal importance, hole injection barrier should be minimized for efficient device efficiency and overall charge balance. PEDOT:PSS with work function of ~5.2 eV is usually used as hole transport layer for PeLEDs. While the ionization potential of organolead trihalide perovskite materials (5.6–5.9 eV) is deeper than the former, indicating large hole-injection barrier and significant exciton quenching at the PEDOT:PSS/perovskite interface. Kim et al. [46] prepared self-organized buffer hole injection layer (Buf-HIL) composed of PEDOT:PSS and a perfluorinated polymeric acid, tetrafluoroethylene-perfluoro-3,6-dioxa-4-methyl-7octene-sulfonic acid copolymer (PFI), which could gradually increase the work function to 5.95 eV from the bottom interface to PEDOT:PSS/perovskite interface (Figure 4(a)). The gradient work function could facilitate hole injection more efficiently than the single energy level of PEDOT:PSS and the PFI enriched PEDOT:PSS/perovskite interface could prevent exciton quenching according to the increased photoluminescence lifetime. Correspondingly, the green PeLED (ITO/Buf-HIL/CH₃NH₃PbBr₃/TPBI/LiF/Al) achieved high color purity (543 nm; FWHM ~20 nm) with current efficiency of 0.577 cd A⁻¹, EQE of 0.125% and luminance of 417 cd m⁻², higher than the PEDOT:PSS based group. Also, the electroluminescence spectra of wide wavelength tenability (Figure 4(b)) and flexible device (Figure 4(c)) have been demonstrated.

Mora-Sero *et al.* [47] studied the stability of bright solid state LEDs. In the air, the electroluminescence signal disappeared in 2 min; under inert condition, the signal decreased slowly and could maintain 300 min under continuous



Figure 3 (a) Structure of PeLEDs with Ca and Ag top electrodes and its energy-level diagram; (b) band diagram of PeLEDs based on ZnO doped with 40% Mg²⁺, showing no electron injection barrier [44] (color online).



Figure 4 (a) Schematic energy-level diagram of ITO/Buf-HIL/CH₃NH₃PbBr₃; (b) electroluminescence spectra of PeLEDs based on Buf-HIL and CH₃NH₃PbCl₃Br₃I_{3-x-y}; (c) flexible green-emitting PeLEDs on PET substrate [46] (color online).

operation. The increase of the non-radiative recombination was responsible for the decay, rather than perovskite material degradation. Increasing the air-tolerance and lifetime is a real challenge for practical PeLEDs.

Due to the success of PeLEDs and perovskite solar cells, integrating both functions in a single device is on the agenda. Gil-Escrig et al. [48] reported CH₃NH₃PbI₃ based planar diode structures (ITO/PEDOT:PSS/p-TPD/CH₃NH₃PbI₃/ PCBM/Ba-Ag) that can convert light to electricity and the reverse. Under AM 1.5 illumination, the device achieved promising solar energy conversion efficiency of 12.8%, while with 2.5 V voltage, and the electroluminescence intensity of near infrared reached 770 µW cm⁻² via pulsed driving. The low EQE (0.04%) of electroluminescence might originate from the low photoluminescence quantum yield (PLQY) of CH₃NH₃PbI₃ and the unpreferable energy barrier for electron injection. In addition, the film thickness of CH₃NH₃PbI₃ is preferable for heterojunction solar cells considering light-harvesting and charge separation, but it might not be preferable for electron-hole recombination in PeLEDs. This work indicates the possibility of integrating multifunctional perovskite based devices, more structure innovation is on the way.

3 Organolead trihalide nanomaterials for lightemitting devices

Solution-processed perovskite film is easy to prepare via spin-coating and annealing. Vapor based approaches and two-step process were employed to further control the perovskite crystallization and morphology, but the former requires dedicated equipment and the latter requires much longer time [49]. Moreover, due to the crystallization process and methylammonium halides sublimation during annealing, it is not easy to form uniform and pinhole-free crystalline thin films, which lead to sub-band defect states and non-radiative pathways. PeLEDs based on perovskite thin film exhibited bright electroluminescence emission only under high current density [50]. Size controlling to the nanoscale and surface vacancies passivation of perovskite nano-species might help overcome the problem [51–53].

To understand the formation mechanism, Yang et al. [54] found that in situ transformation and dissolution-crystallization mechanisms play competing roles in determining the characteristics of products. Controllable morphology of CH₃NH₃PbI₃, such as cuboids, rods, wires and plates, could be achieved by controlling reaction kinetics. To the nanoscale, capping agents and solvents with varying polarities were involved to control the size, morphology and crystallization, together with tunable emission spectrum. CH₃NH₃-PbX₃ (X=Cl, Br, I) have been developed to various nanocrystals, including nanoparticles, nanodots, nanorodes, nanosheets, nanoplates, nanowires, and so on [55,56]. Zhang et al. [57] reported ligand-assisted reprecipitation for brightly luminescent colloidal CH₃NH₃PbX₃ (X=Cl, Br, I) quantum dots (QDs), and their photoluminescence spectra can be finely tuned from 407 to 734 nm (Figure 5) with absolute PLQYs of 50%-70% at room temperature. The colloidal CH₃NH₃PbBr₃ QDs with saturated green emissive were applied to GaN excited white LED and the device achieved luminous efficiency of 48 lm W⁻¹ with coordinate



Figure 5 (a) Optical images of CH₃NH₃PbX₃ QDs (No. 1–9) under ambient light and a 365 nm UV lamp; (b) photoluminescence emission spectra of CH₃NH₃PbX₃ QDs [57] (color online).

of (0.33, 0.27).

In 2015, Li *et al.* [58] prepared a blend of CH₃NH₃PbBr₃ nanocrystal and a polyimide precursor dielectric (PIP) for LEDs (Figure 6), where the former forms electrical contact with the electron- and hole-injection layers and the PIP layer forms a pinhole-free charge-blocking layer. This green device achieved an external quantum efficiency of 1.2% due to reduced non-radiative current losses and improved quantum efficiency. Additional benefit is the flexibility of polymer matrix, which may be beneficial for flexible lightering displays.

With simple device architecture and easy preparation, light-emitting electrochemical cells (LECs) can be potential alternative to LEDs. For the first time, Aygüler *et al.* [59] reported LECs (Figure 7(a)) based on perovskite nanoparticles by spray-coating. They demonstrated that FAPbBr₃ nanoparticles exhibited lower radiative bimolecular recombination rate than that of CH₃NH₃PbBr₃ nanoparticles. With perovskite NPs and polyelectrolyte matrix (LiCF₃SO₃ and trimethylolpropane ethoxylate) as the luminescent layer, the device showed no change in shape and maximum under different applied voltages (Figure 7(b)). The green LECs achieved stable luminance of 1–2 cd m⁻² at low driving currents and stability of over two months stored under ambient conditions (Figure 7(c)).

4 Summary and perspectives

Recent studies have demonstrated that organolead trihalide perovskite materials are promising candidates for efficient LEDs, which opened a door toward novel solid lighting and display devices. The PeLEDs featured several aspects that are worth of further studies, including: (1) facial solution-



Figure 6 (a) Device structure of PeLED based on CH₃NH₃PbBr₃ nanocrystal: PIP composition; (b) image of green PeLED [58] (color online).

process fabrication at low temperature; (2) highly bright and pure electroluminescence with tunable spectrum; (3) various active materials selection and controllable interface engineering for further improvement. On the other hand, some main concerns about PeLEDs related to future development and practical applications are prominent, including:

(1) Device performance. Recent PeLEDs exhibit inferior performance parameters compared to other LED types, including luminescence, current efficiency, and EQE. Due to the high photoluminescence yield (up to 70%) of perovskite thin films [50], there is much room for improvements. New strategies for high-quality perovskite thin film and nano/ micro crystals are crucial for device performance. Selections of transporting materials and control of interface engineering could also play significant roles. Intrinsic whitelight emission of layered hybrid perovskite was observed [60], which indicates the possibility of white light-emitting with only perovskite materials.

(2) Stability and lifetime. Since the organolead trihalide perovskite materials are sensitive to moisture and organic/ polymeric transporting materials may suffer from de-doping or phase separation in the long run, the stability of PeLEDs is far from acceptable level. Also, deep insight into the device degradation mechanism is needed with focus on the non-radiation approaches. The same problem took place for many devices at initial stage, we believe this concern will be solved via optimized materials, well-designed structure and protective packages in the near future.

(3) Structure innovations. Due to solution processable fabrications at low temperature, light emitting devices based on perovskite materials, including LEDs and LECs, have great chance for flexible or even stretchable applications. Except for traditional substrates, micro/nano-structured electrodes could increase optical outcoupling, and other substrates (like wires or balls) might potentially extend the devices to some really special applications. Further, integrating perovskite thin film or nanostructures based LEDs to classical light emitting devices and thin film transistors would provide wide chance for new generations of light sources.

(4) Environmental considerations. It is no wonder that organolead trihalide perovskite based devices would suffer from lead pollutions. But the negative effects could be minimized via recycling the lead components. Sn^{2+} substituted CH₃NH₃Pb_{1-z}Sn_zX₃ (*z*=0–1; X=Cl, Br, I) species could further reduce Pb amount of PeLEDs and extend the emis-



Figure 7 (a) Illustration of the LEC device; (b) 3D plot of electroluminescence spectra at different applied voltages of FAPbBr₃-based devices; (c) electroluminescence spectra of both fresh and two month old FAPbBr₃-based devices obtained at the maximum luminance level [59] (color online).

sion wavelength to ~1000 nm [61], and the metallic nature of the Sn based perovskite might have special effects on the device performance. Another analogue, $CsSnI_3$ with bandgap of 1.3 eV [62] could avoid organic species and might play a role in PeLEDs.

Due to the rapid revolution of light emitting devices, PeLEDs would boom up in the immediate future, which also inspire the exploration of perovskite materials for other optoelectronics.

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Conflict of interest The authors declare that they have no conflict of interest.

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