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Latest advances in perovskite LED research

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Abstract. In recent years, there is a growing need for a better performance, lower cost, brighter and longer life luminous and display technology. Perovskite materials have attracted widespread attention because of their excellent performance in optoelectronic devices. For example, it has high carrier mobility, small emission line width, bandgap tunability, and strong photoluminescence quantum yield (PLQY). As a result, perovskite light-emitting diodes (LEDs) have developed rapidly over the past few years. This article starts with the basic parameters of perovskite LED (PeLED) devices and describes the basic structure and working principle of perovskite LED devices. And it mainly reviews the development history of 3D perovskite LEDs and states the latest progress in the research of perovskite quantum dots (QDs) and hole transport layers (HTLs) and electron transport layers (ETLs) in perovskite LED devices. Finally, the problems restricting the development of perovskite LEDs are summarized. This article offers a comprehensive understanding of perovskite LED devices and their future research directions.

Keywords: perovskite LED, quantum dots, ETL, HTL.

1. Introduction

With the development of today's display technology, people increasingly need high-efficiency, environmentally friendly, low-cost, long-life luminescent materials and devices. The excellent properties make perovskite LEDs become today's light-emitting devices with great potential. LEDs are now widely used in lighting, display, and communication fields.

1.1. Basic parameters of LED devices

The ratio of the number of photons emitted by the diode to the number of carriers injected into the device is defined as the external quantum efficiency (EQE), and the photoelectric performance of the device is measured by EQE. Luminance is used to represent the luminous intensity per unit projected area. The full width at half peak (FWHM) is used to represent the peak width of the spectrum at a height of half the peak. Electroluminescence spectroscopy (EL) is used to describe the wavelength vs. intensity of the light emitted by LED devices. The operating voltage of the device at a brightness of 1cd m^{-2} is defined as the turn-on voltage. The time elapsed when the operating brightness of an LED device drops to half of the initial brightness is defined as the operating life of the LED (T50). These parameters can describe the performance of a certain LED device.

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1.2. The basic structure of perovskite LED

Perovskite LEDs adopt a "sandwich" device structure. Its main structures include a cathode, anode, ETL, HTL, and light-emitting layer. Perovskite LED is named because its light-emitting layer is composed of perovskite materials.

1.3. The working principle of perovskite LEDs

Perovskite luminescence is generally divided into photoluminescence and electroluminescence. In general, if a perovskite crystal is irradiated by a photon whose energy is greater than the semiconductor band gap, the electron will transition from the valence band to the conduction band. The electrons in the conduction band return to the valence band and recombine with the holes, which will produce photons of a specific wavelength, which is the photoluminescence of perovskite crystals [1]. But perovskite LEDs work by electroluminescence. When an applied voltage is applied across the perovskite LED device, the hole will enter the hole transport layer through the anode, and the electrons will enter the electron transport layer through the cathode. Then the electrons and holes enter the perovskite light-emitting layer from the electron transport layer and the hole transport layer, respectively, to form high-energy excitons, and finally return to the ground state and release photons [1,2]. The schematic diagram is shown in Figure 1.

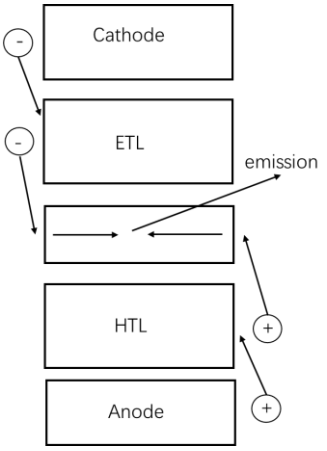

Figure 1. Structure of perovskite LED.

2. Light emitting layer based on perovskite materials

2.1. The development history of 3D perovskite LEDs

Perovskite LEDs are classified according to the spatial dimension, which can be divided into four categories, namely 3D, 2D, 1D, and 0D perovskite materials. Because 1D perovskite materials have structural limitations, they have been poorly studied [3].

The 3D perovskite material has a cubic crystal structure, and the chemical formula of its unit cell is ABX_3, with the A cations occupying the corner sites, the B cations occupying the body center, and the X anions occupying the face centers. And A is an organic group or cation, B is a metal cation, and X is a halogen anion [3]. The Goldschmidt tolerance factor (t) and the octahedral factor (μ), which are obtained using Equations (1) and (2), respectively, determine the creation of a stable 3D cubic phase. The effective ionic radii of A, B, and X in the perovskite are, respectively, R_A, R_B, and R_X.

$$t = \frac{R_A + R_x}{\sqrt{2}(R_B + R_x)} \tag{1}$$

$$\mu = \frac{R_3}{R_x} \tag{2}$$

When the value of t is between 0.8 and 1, the perovskite structure formed can remain stable at room temperature [4]. If the calculated t-value is between 0.9 and 1.0, this means that this perovskite structure is cubically symmetric, and stable [5]. When t is no longer within this range, other structures appear. If

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t is much greater than 1 or less than 0.7, no 3D perovskite structure will be formed [5]. Therefore, perovskites with a stable structure can only be obtained by selecting components with suitable ion radii [5]. And the ideal high-symmetry cubic phase ABX_3 perovskite will also undergo lattice structure distortion due to changes in external conditions such as external pressure and temperature, and transform from cubic phase to low-symmetry structures such as tetragonal phase or orthorhombic phase [5].

Tan et al. published the first study on 3D HPLEDs. They created an infrared LED device with a structure of indium tin oxide (ITO)/TiO_2/$CH_3NH_3PbI_{3-x}Cl_x$/F8/MoO_3/Ag. According to reports, it had internal and external quantum efficiencies of 0.1% and 0.4%, respectively [6]. This is mainly because at that time in the early stage of high-performance LEDs (HPLEDs) research, the quality of perovskite films was not high, so the electroluminescence performance of the device was not ideal [7]. Although the performance of the device they prepared is not superior, even far lower than the traditional inorganic or organic LED, as the first to prepare perovskite light-emitting devices that can work at room temperature and the first application of 3D HPLEDs, this has greatly attracted people's attention, stimulating people's research enthusiasm, and is a turning point in the research of PeLEDs [6,7]. Since then, perovskite LEDs have developed rapidly.

2.2. Research progress of perovskite quantum dot LEDs

Tang et al. optimized the luminescence characteristics of the emission layer material from the two aspects of material and device physics, and they also improved the carrier balance of the device, thereby improving the efficiency of the electric perovskite LED. They used the short-chain organic ligand p iodine-d-phenylalanine (PIDP) to post-process $CsPbI_3$ QDs to optimize the photoelectric performance of the light-emitting layer material [2]. To facilitate the carrier transport of the light-emitting layer of LED devices, the conductivity of perovskite QD films was increased by partially substituting ligands such as oleamine and oleic acid [2]. According to their research, PIDP successfully passivated the defects on the perovskite surface, increasing its PLQY [2]. Finally, they successfully prepared a perovskite LED device with an external quantum efficiency of 12.4% and a maximum luminance of 2000 cd m^{-2} [2]. They also appropriately adjusted the carrier mobility of the device transport layer material, which improved the carrier injection balance of the light-emitting layer of the perovskite LED device [2]. They doped Co into ZnO, improving the carrier injection balance of the $CsPbI_3$ QD LED. At the same time, the luminance efficiency of the perovskite light-emitting layer was improved [2]. They found that doping Co into ZnO also improved the film-forming performance of the perovskite light-emitting layer, which was conducive to the preparation of high-efficiency LED devices [2]. They increased the EQE of the $CsPbI_3$ QD LED by 70% and the maximum brightness to 1858 cd m^{-2} [2].

Tang et al. used $ZnBr_2$ as a surface ligand for $CsPbBr_3$ QDs and applied it to electroluminescent QLED devices [4]. The outcomes of the experiments demonstrate that the $ZnBr_2$ ligand alteration can greatly lower the non-radiative recombination centers on the surface of QDs, which is advantageous for charge transfer in QDs films [4]. They used the $CsPbBr_3$ QDs of $ZnBr_2$ ligand modification as the light-emitting layer to prepare ITO/ Poly(3,4-ethylenedioxythiophene) /poly(styrenesulfonate) (PEDOT: PSS)/Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine (PTAA)/QDs/TPBi/LiF/Al structure QLED devices with a maximum luminance of 16130 cd/m^2, which was 335% higher than unmodified QDs devices [4]. The external quantum efficiency was 7.74%, which was 63% higher than that of unmodified QDs devices [4]. Additionally, they carried out research on the manufacturing of sodium-ion-doped $CsPbBr_3$ quantum dots and used them in QLEDs. They investigated how the optical and electrical characteristics of $CsPbBr_3$ QDs were affected by various Na^+ ion concentrations [4]. The experimental findings indicate that the maximal quantum efficiency was 94.74% when the Na/Cs ratio was 1/3 [4]. Its undoped values were 77.34%, 30.4 s^{-1} for radiation recombination, and 31.2 ns for fluorescence lifetime. They created electroluminescent QLED devices using the Na^+ -doped $CsPbBr_3$ QDs as luminescent components [4]. A maximum brightness of 20190 cd/m^2, maximum current efficiency of 34.5 cd/A, and external quantum efficiency of 8.97% were all achieved by the device [4].

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3. Hole transport layer

Perovskite materials have great application prospects in light-emitting devices. However, there are also some problems in LED devices, such as in HTL, which has the problem of carrier transport mismatch, so it is urgent to enhance the transmission capacity of the hole transport layer. PEDOT: PSS is a common conductive polymer which is widely used as HTL materials in various optoelectronic devices. Despite some limitations, its charge carrier mobility, chemical stability and morphology can be improved through modification. Mei et al. improved the photoelectric performance of PeLEDs by using a composite hole transport layer and other means [8]. They introduced molybdenum trioxide (MoO_3) into PEDOT: PSS to construct a composite hole-transporting layer. Her research indicates that a volume ratio of 1:0.02 between molybdenum trioxide and PEDOT: PSS was ideal [8]. Based on the modified HTL, the maximum luminance reached 5044 cd/m^2 and the maximum current efficiency reaches 3.12 cd/A [8]. By observing the results of the experiment, they concluded that an appropriate amount of molybdenum trioxide can help improve the quality of perovskite films, enhance the hole-transporting ability of the composite hole transport layer, match carrier transport, and improve the photoelectric performance of the device [8]. To form a composite hole transport layer, they also added Graphene oxide (GO) to PEDOT: PSS. Their research shows that the ideal volume ratio for PEODT: PSS and GO was 1: 0.3, and that the maximum device luminance and current efficiency were 3302.66 cd/m^2 and 1.91 cd/A, respectively [8]. The experimental findings demonstrate that adding the right quantity of GO can enhance the hole injection capability, perovskite thin film quality, and electrical performance of the device [8].

Zhang et al. studied the effect of adding different masses of $Mg(CH_3COOH)_2•4H_2O$ to the hole transport layer PEDOT: PSS (4083) on the topography of the light-emitting layer, and found that the band gap of the hole transport layer could be adjusted, the bandgap matching degree and the carrier transport balance could be promoted by adding $Mg(CH_3COOH)_2•4H_2O$ [9]. Based on the above research and some other studies, they prepared metal halide perovskite blue LEDs doped with inorganic substances in the hole transport layer with high brightness and high stability [9].

Wu et al. optimized the hole transport layer by using alcohol-based solvents to prepare PeLEDs with better performance. They studied the effects of three high-polarity solvents, methanol, ethanol and isopropanol, on the hole transport layer and the perovskite luminescent layer [10]. Their research shows that the treatment of alcohol solvents could improve the hole transport capacity of the device and the crystallinity of the perovskite, which in turn enhanced the radiation recombination ability of excitons [10]. The maximum luminance of the PeLEDs device was 2075 cd/m^2. Maximum current efficiency and power efficiency both rose over those of the control group by roughly 40 and 10 times, respectively [10]. The turn-on voltage of PeLEDs could be efficiently decreased by alcohol solvent treatment at the same time [10]. They optimized the hole transport layer with methanol solvent to prepare a multifunctional optoelectronic device. The luminance of the multifunction device can reach 13737 cd/m^2 [10].

4. Electron transport layer

The selection of the electron transport layer determines the balance of holes and electrons in the device, which will directly affect the performance of the device, so the selection and optimization of the ETL is crucial [11]. Zhang et al. selected three materials, Bphen, TPBi and TmPyPB, which are often used as electron transport layers of PeLEDs, and prepared each electron transport layer by solution method and vacuum evaporation method, respectively, and then prepared different electron transport layer devices, and compared the performance of different electron transport layer devices. Based on the experimental results, they found that the perovskite light-emitting diode with Bphen as the electron transport layer had the best performance when preparing electron transport layer devices using the solution method [11]. The turn-on voltage of the device was 2.6 V, the maximum luminance was 9641 cd m^{-2}, and the maximum current efficiency was 1.32 cd A^{-1} [11]. According to analysis, the reason is that Bphen has a relatively high electron mobility that matches PEDOT: PSS with no electron injection barrier [11]. However, the luminance and current efficiency of TPBi and TmPyPB devices was not high. The performance of devices prepared by vacuum evaporation and solution method was similar, while the

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solution method to prepare Bphen electron transport layer was more suitable for their devices, so they optimized the concentration and spin coating speed to improve the device performance. The experimental results show the best concentration of Bphen is 10 mg mL^{-1}, and the best spin-coating speed is 2000 rpm [11].

Zhang et al. attempted to create an ETL using one-dimensional TiO_2 nanorod arrays and zinc sulfide (ZnS) semiconductor materials, and to study the regulation of halogen hybrid perovskite ($CH_3NH_3Pb(Br_xCl_{1-x})_3$) material synthesis. They first synthesized $CH_3NH_3Pb(Br_xCl_{1-x})_3$ material in the early stage, and then prepared TiO_2/ZnS composite film by drop-coating method, and then dripped coated the previously synthesized $CH_3NH_3Pb(Br_xCl_{1-x})_3$ material to prepare TiO_2/ZnS/perovskite composite film [12]. They then tested and assessed the performance of these films. The researchers discovered that the composite thin film created by dispensing 20 μL of a mixture of naphthol, 100% ethanol, and ZnS showed good optical and electrical characteristics, a comparatively high photocurrent, and a consistent response curve [12]. In the template and reaction time control groups, they discovered that the composite film corresponding to zinc sulfide produced at 180 °C reaction without template agent displayed good photoelectric capabilities, indicating that the composite film was more applicable as an electron transport layer [12]. By drop-coating with the above-mentioned halogen hybrid perovskite powder to create a mixed solution, they created TiO_2/ZnS/perovskite composite films. The perovskite obtained on the zinc sulfide layer expanded to a size of more than 10 μm after the perovskite layer had been annealed. In the 200–800 nm region, the UV–Vis absorption spectrum of composite films displayed a step-like decreasing trend [12].

5. Conclusion

Perovskite materials have excellent photoelectric properties. Therefore, it has great development prospects in many optical devices and electronic devices. In the research of perovskite quantum dot LEDs, they mainly optimize their performance from the aspects of materials and device physics, among which the research is mainly carried out by using different ligands. In the study of the hole transport layer, researchers mainly study by adding other substances to PEDOT: PSS to form a composite hole transport layer. For the electron transport layer, researchers mainly study the performance of different materials and devices prepared by different methods. This article mainly introduces the latest development of perovskite LED device research by researchers. Although perovskite LEDs have broad development potential, they also have considerable limitations at present. There are two main factors restricting the commercialization of perovskite. One is the instability of the perovskite material itself, and the other is the instability generated during the operation of LED devices. In future practice, researchers may mainly study 2D perovskite materials and LED device encapsulation techniques to further improve stability.

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