The Design and Progress of Organic Light-Emitting Diode

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Abstract: Organic light emitting diode (OLED) is one of the main lighting devices and can be used as mobile phone screens, so its performance enhancement is worthy of an in-depth study. This paper discusses three types of devices with different light emitting principles in the history of OLED development in chronological order and their performances, as well as ways to enhance their external quantum efficiency (EQE). For fluorescent, phosphorescent and thermally activated delayed fluorescent (TADF) OLEDs, adding additional layers and doping are effective means of improving the performance. For fluorescent OLED, the EQE can be increased up to 11.5% by adding an efficiency enhancement layer and doping the emitting layer with a new blue dopant with a higher orientation coefficient. For phosphorescent OLED, a hole transport layer is utilized to block excitons within the FIrpic-doped emissive layer leading to an EQE of 16.7%. For TADF OLED, the soluble doped TADF OLEDs is helpful at improving the quantum efficiency up to 18.3%. This paper looks forward to the maturation of these strategies and their practical application, and the identification of more technologies that can enhance the performance of OLED devices to help make it more usable.

Keywords: Emissive Layer, OLED, External Quantum Efficiency.

1. Introduction

Since the practical organic light emitting device (OLED) was first invented in 1987, OLED has demonstrated its advantages over regular LEDs. Light is produced in OLEDs when current passes through a film of organic material which is the emissive electroluminescent layer. OLED has been regarded as one of the most promising display technologies due to the fact that it provides a new dimension to this field. OLED has a number of advantages over conventional LEDs, including superior display quality, flexible displays, a wide viewing angle, and a wide range of colors, etc [1]. Compare to inorganic LEDs, OLEDs are thinner and lighter, and more approachable in industrial fabrication. Due to the great potential of OLEDs for commercialization in the form of screens for electrical devices and panel displays, researchers have studied for decades to the task of enhancing the capabilities of these devices. Over the last few decades, fluorescent, phosphorescent and TADF materials have been discovered and applied to OLEDs, significantly enhancing OLED performance and helping to bring OLEDs into applications.

A large body of literature has accumulated a wealth of experience through experiments and data measurements on different aspects of device structure enhancement over the last decade. However, the three different light emitting principles in the development of OLED need to be systematically summarized and integrated in order to indicate future improvement directions for structural materials with different advantages and disadvantages.

The main objective of this paper is to analyse the methods and ideas used to improve the performance of three different light-emitting principles in the development of OLED. Firstly, the OLED device structure and its working principles are presented in detail. Then the physical characteristics and development history of the three different OLED light-emitting principles are listed in chronological order, their physical limitations are analysed, and different techniques and ideas to improve their performance are demonstrated. By manipulating the device structure like adding new layers and doping, the device performance has significantly improved and specific experimental data are presented in comparison with unmodified devices. Finally, the current obstacles to future development and possible ways to improve OLED are summarised.

2. The device structure and its working principle

OLED consists of an emissive layer (EML) and conductive layers. The basic structure is shown in Figure 1, the layers are placed on a substrate in between the anode and cathode, creating a sandwich structure, which forms the basic structure of OLED. Light is generated by the flow of electrical current, and the process that generates light makes use of organic substances. Brightness and colour of light are controlled by increasing material qualities; colour can be altered by modifying the molecular structure; brightness can be altered by modifying the molecular structure, device structure, voltage, and current.

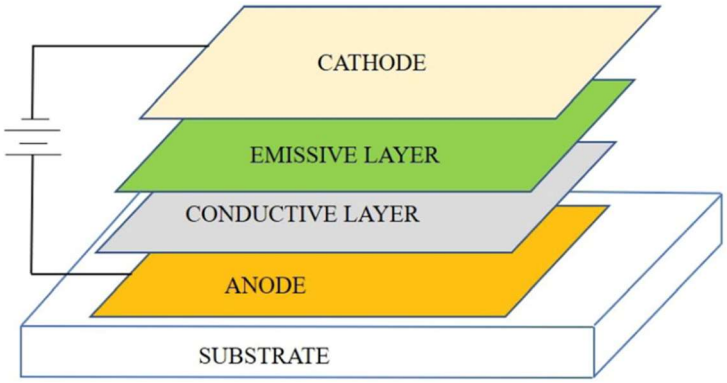


Figure 1. The basic structure of single-layered OLED (Photo credit: Original).

OLEDs produce light through a process known as electron-hole recombination. Charge carriers must first be injected, then transition, and finally recombine, in order for light to be emitted. The difference in work function between an electrode and an organic semiconductor has an effect on charge carrier injection. It is necessary to introduce charge carriers into an organic semiconductor in order to facilitate recombination, which takes place in the emissive layer. Light is produced in recombination process.

In a practical sense, recombination may not be gauranteed to occur within the emissive layer because there is a difference in the mobility of electrons and holes. The hole mobility is typically higher than the electron mobility in most of organic materials, as a result, all of the recombination takes place in close proximity to the cathodes [2]. Therefore, in order to let two charge carriers own the same mobility, more layers are introduced into the device structure: the transport and injection layer; they are essential in piratical use. It is important that the emissive layer keep a high quantum efficiency while also maintaining mobility and having improved hole and electron injection. Therefore, multi-layered structure is also used to enhance parameters. Because energy levels should be roughly matched; otherwise, the performance of the device may deteriorate as a result of low charge carrier injection. Therefore, the solution to the problem of lowering the energy barrier is to include transport layers in the structure that lies between the emissive layer and the cathode and anode. Because of the band offset, these layers boost electron mobility while simultaneously decreasing the hole current in the OLED.

Furthermore, because of the energy barrier that exists between the transport layers and the electrodes, only a negligible amount of charge carriers are allowed to enter the device. Thus, injection layers are introduced to inject and transport the charge carriers. To minimise the energy barrier, an intermediate energy level is created and the work function of the electrode is determined. Thus, to enhance the properties of OLED, the multi-layered structure is utilized to improve parameters. As can be seen from Figure 2, the electron and hole transport layer (ETL/HTL) and electrons and hole injection layer (EIL/HIL) are incorporated between the anode and cathode. As a result of their greater mobility, holes travel quicker than electrons and reach the emissive layer prematurely. Consequently,

recombination does not occur correctly. The hole blocking layer (HBL) is added to limit the mobility of holes and match that of electrons.

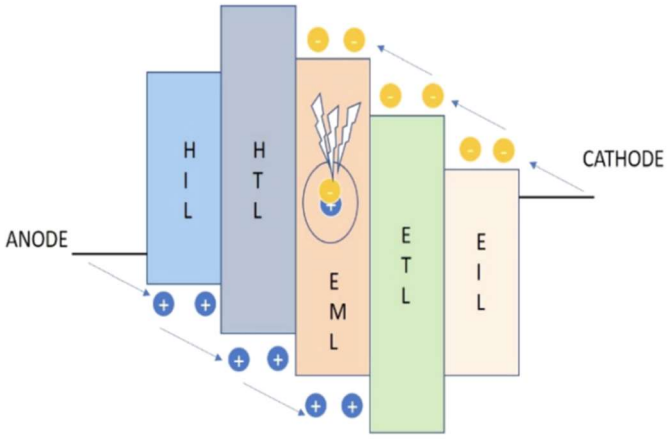


Figure 2. The structure of OLED with transportation and injection layers (Photo credit: Original).

3. Fluorescent OLED

Fluorescence is one of the most typical light-emitting methods of OLED and is also the earliest of all light-emitting methods of OLED to be developed, and its industry is the most mature. Under electrically excited conditions, the chances of holes and electrons combining to form singlet excitons and triplet excitons are 25% and 75%, respectively. Due to the fact that it is only possible to utilise the produced singlet excitons in fluorescent materials through the process of singlet-singlet energy transfer, devices that are made from singlet state light-emitting materials with internal quantum efficiency at its greatest level of 25% [3]. Two strategies were applied to fluorescent OLED in 2014 to help improve its external quantum efficiency (EQE).

In order to have a higher EQE, having a larger singlet exciton formation ratio and out-coupling efficiency is the key. This is something that can be accomplished by triplet-triplet fusion (TTF) and by properly aligning the molecules orientation that make up the fluorescence emitter. The TTF model depicts the behaviour of triplet excitons created in an organic layer. When triplet excitons collide with one another, singlet excitons are produced as a result of their interactions. This indicates that one singlet exciton can be created by the combination of five triplet excitons. Since this is the case, besides the singlet excitons that were initially formed of 25%, there would be an extra 15% of singlet excitons generated. This indicates that the utilisation of this phenomena would result in a 40% increase in the creation of singlet excitons. Due to the fact that the amount of singlet excitons produced is relevant to the density of triplet exciton, in order to reach a higher degree of productivity and efficiency, it is very necessary for triplet excitons to be contained within the EML.

In fluorescent OLEDs, triplet‑triplet annihilation methods have obtained EQEs of 11.5% and 8.6% for red and yellow light respectively[4], by placing an additional assisting layer between the EEL and ETL, the assisting layer contains a blue host material and a green dopant. However, as green component is present in the device, it will be hard to apply the assisting layer technique to enhance the EQE of blue OLEDs. Therefore, considering the TTF in OLEDs' working mechanism, a blue fluorescent system was created by inserting an undoped efficiency-enhancement layer (EEL). Additionally, electron-transporting materials in pure blue fluorescent OLEDs were found to produce an EQE of over 10%.

To be able to restrict the triplet excitons, it is necessary to have an HTL material and an EEL material, both of which have a greater triplet level than the emitting materials. EEL-2, a newly synthesised EEL material, exhibits an electron mobility of around 104 $cm^2V^{-1}s$ and an electron affinity level about identical to the blue host material [4].

Molecular orientation is another strategy for promoting OLED efficiency. Studies have been done on particular molecular arrangement that display a horizontal orientation. Moreover, There are some host materials and dopant materials that, when used in blue fluorescence devices, exhibit molecular orientation. This results in high quantum efficiencies in both doped and undoped devices. In blue OLEDs, BDs with greater ovality result in a higher orientation factor and EQE [5]. Additionally, it was discovered that the extent of EQE enhancement depends solely on the enhancement of outcoupling efficiency by the BD orientation. In order to improve the TTF process, an EEL with greater triplet energy was added, and new dopant with higher orientation factors were created. The EQE was enhanced by up to 11.5% as a result. A parallel-oriented blue dopant's improved outcoupling efficiency was the cause of the high EQE value. Overall, the findings result in EQEs for luminous blue emitters that are higher than 14% [5].

4. Phosphorescent OLED (PHOLED)

Triplet excitons have a long lifetime and phosphorescence is difficult to detect in OLEDs that exclusively use fluorescent organic molecules because it is quantum mechanically impossible for triplet excitons to decay considering selection rules. Therefore, in fluorescent OLEDs, the emission of useful light only occurs in the presence of singlet excitons, setting a theoretical ceiling of 25% for internal quantum efficiency [6]. Phosphorescent OLEDs, on the other hand, light is generated from both triplet and singlet excitons, enabling such devices' EQE to approach 100%. PHOLEDs are being researched for prospective application in general lighting requirements as well as large-screen displays due to their possibly high energy efficiency than other OLEDs. The PHOLEDs also distribute light equally and save energy massively. While the PHOLEDs still suffering from short operational lifetime caused by different average lifetimes for three colors. Due to the fact that red and green PHOLEDs often have lives that are longer than lives of blue ones, practical displays would visually deformed quickly which would not be appropriate for an OLED that is economically viable. A new device FIrpic-based phosphorescent OLED with high efficiency using the host material SiCa is created. This device exhibits high efficiencies of up to 18.3% [7]. The two strategies of improvement in 2015 are (a) DTAF effectively occluded and contained excitons in the emissive layer, and (b) a DPPS layer prevents exciton quenching at the interface of EML and ETL. The triplet energy must be strong enough to restrict triplet excitons for highly effective blue PhOLEDs. Triplet excitons must not diffuse into non-radiative HTL or electron ETL levels. For blue PHOLEDs to be truly effective, charge recombination efficiency must be significantly increased. This can be accomplished by employing charge-transporting materials that are particularly effective in order to preserve charge equilibrium and contain triplet excitons in the emissive layer. To improve the EL efficiencies, a newly developed material DTAF is using as the HTL. The molecular arrangement of DTAF has several advantages like its high morphological and thermal stability; high hole transport properties; and a wide triplet energy gap. Due to the advantages listed above, it is able to provide a lower barrier of hole injection from the anode, weaken electron injection from the cathode, and confine triplet excitons within the EML. These benefits are all possible because of the structure of the EML. Moreover, in order to prevent the FIrpic exciton from being quenched at the interface of EML and ETL, a layer of DPPS is placed. This exciton and HBL layer serves as a buffer between the two layers. The above strategies lead to EQE of 18.3% and the EQE continued to be as high as 16.7% even when the brightness was up to 1000 cd/m^2 [8].

5. Thermally activated delayed fluorescent (TADF) OLED

While shortcomings exist in fluorescent OLEDs and phosphorescent OLEDs, because electro-excitation can only result in the generation of a quarter of the singlet excitons, the FOLED technology is restricted as a result of this low 25% EQE. Phosphorescent materials are able to circumvent this constraint by including metal components such as Ir and Pt; nevertheless, PHOLEDs run into issues in the deep blue area due to the short device lifetime, indeterminate toxicity, and high manufacturing

cost. The E-type delayed fluorescence, which was renamed thermally activated delayed fluorescence (TADF) in 2012, is one approach that has been investigated as a potential solution [9]. The most commonly used fabrication technique is the vacuum deposition method. However, by using this technique, the severe conditions contribute to the level of difficulty associated with the production process, like absolute vacuum and high temperature, and a decrease in the amount of OLED materials that are utilised. In addition to this, it is extremely challenging to deposit many components simultaneously in the same layer while maintaining the layer's precise composition. Additionally, producing devices with a wide surface area is tough as well because of the difficulty in making high-resolution colour pixel patterns with a fine metal mask. This presents a complication in the manufacturing process. Because of these factors, the process of industrialising vacuum-deposited organic light-emitting diodes is difficult.

Instead of fabricating OLEDs by the vacuum deposition method, solution-processing methods is in advance in many aspects. It can provide some special benefits like low manufacturing costs, high processing effectiveness, compatibility with flexible substrates, comparatively little waste material, and superior doping concentration control. However, vacuum-deposited OLEDs still outperform solution-processed OLEDs when considering device performance, therefore solution-processed OLEDs still need to improve in this area.

Furthermore, soluble TADF materials were synthesised to develop highly efficient solution-processed TADF devices [10]. Tert-butyl modification of the 4CzIPN dopant was found to boost TADF dopant solubility while maintaining the film form of the emitting layer in the devices. This was discovered through experimental research. As a consequence of this, it was successful in raising the EQE of solution-processed devices, and it was able to increase the EQE of green devices that utilised the t4CzIPN dopant by as much as 18.3%. Doping with the t4CzIPN, soluble TADF OLEDs have a quantum efficiency that was equivalent to the quantum efficiency of TADF devices with vacuum-deposited production with the same doping material.

6. Conclusion

Due to the irreplaceable nature of OLED for applications such as mobile phone screens and lighting devices, methods to enhance OLED with different luminescence principles are well worth investigating in depth. This article lists three light-emitting principles in the history of OLED development: fluorescent, phosphorescent and TADF OLED; and two ways to enhance device performance: adding a new layer and doping. In the case of fluorescent OLED, the physical properties dictate a maximum EQE of 25%, so an eficiency enhancement layer and a newly investigated blue dopant with a high orientation coefficient was introduced, the two strategies raising the EQE to 11.5%. For phosphorescent OLED, the physical characteristic allows it to have a high IQE up to 100%, while it still suffering from short operational lifetime caused by different average lifetimes for three colors. Thus, in DTAF based OLED, HTL can be employed to prevent excitons in the emissive layer, and a DPPS layer can be used to suppress FIrpic-induced, leading to an EQE of 16.7%. Then considering the TADF OLED, the soluble TADF devicess with t4CzIPN as dopant improve quantum efficiency, with a high EQE of 18.3% reported in green TADF devices. Beside the EQE of OLED devices, material properties, lifetime, resistivity and current density also needs to be considered in the application for further improvement. TADF devices can exhibit 100% quantum efficiency, but needs further research on its lifetime and colour purity. This paper summarizes and concludes the contribution of different strategies to the performance enhancement of OLED and indicates the future development of OLED devices.

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