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SPECIAL ISSUE: Flexible and Stretchable Energy

Highly efficient inverted organic light-emitting diodes based on thermally activated delayed fluorescence

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ABSTRACT Green inverted organic light-emitting diodes (OLEDs) based on a thermally activated delayed fluorescent (TADF) emitter, 2-pheyl-4'-carbazole-9-H-thioxanthen-9-one-10,10-dioxide, with a cathode of indium tin oxide (ITO)/ZnO injecting electrons efficiently into the electron transporting layer of Alq3, are demonstrated for the first time. The insertion of 7-nm Cs_2CO_3 can further enhance the electron injection. The optimized device with 25-nm ZnO and 7-nm Cs_2CO_3 affords the highest performance of the inverted devices with a current efficiency of 28.1 cd A^{-1}, a power efficiency of 16.1 lm W^{-1}, and an external quantum efficiency of 9.8%. The inverted OLEDs based on TADF emitters are competitive compared with conventional OLEDs because of their air-stable electrodes and TADF emitters, which enable simpler encapsulation.

Keywords: OLEDs, thermally activated delayed fluorescence, inverted OLEDs

Organic light-emitting diodes (OLEDs) have attracted increasing attention because of their advantages of low power consumption, light weight, fast response time, large viewing angle, high brightness, and mechanical flexibility [1–4]. Many efforts have been made to prepare high-performance OLEDs with excellent stability in the past two decades, and some products based on OLEDs have been introduced to the market [5–7]. Nevertheless, their intrinsic low environmental stability requires rigorous encapsulation to enhance their lifetime, which directly increases the final cost of the devices and thus limits the competiveness of OLEDs. Inverted-structured OLEDs have recently been reported as potential substitutes for conventional OLEDs [8–11]. In these devices, air-stable metals with high work functions were used as the anode, indium tin oxide (ITO) was used as the cathode, and air-stable metal-oxide layers were used as the electron-injection layers (EILs) and hole-injection layers (HILs). These metal oxides result in exceptional stability, mechanical and electrical robustness, low cost, transparency in the visible region, and solution-processable fabrication. Thus, the high stability of inverted OLEDs can be expected to fulfill the requirements of real applications. In addition, the inverted OLEDs have a bottom ITO cathode and can be directly connected to the drain electrode of a-Si thin film transistors, facilitating the fabrication of active matrix OLEDs for large-area displays. Although metal oxides can encapsulate the organic emitting layers from oxygen and moisture, the stability and performance of inverted OLEDs are unsatisfactory because of the limited stability of phosphorescent emitters and unbalanced hole and electron injection.

Thermally activated delayed fluorescent (TADF) emitters yield stable fluorescence with very high singlet yields, as these materials exhibit sufficiently small energy gaps between singlets and triplets to enable the up-conversion of triplet excitons to singlet excitons and then realize 100% internal quantum efficiency (IQE) of the singlet excitons formed by electric excitation. Versatile TADF emitters have been reported, including spiro-acridine, triazine, diphenyl sulfone derivatives, and thioxanthone (TX) derivatives [12–15]. OLEDs based on TADF emitters afford high

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external quantum efficiencies (EQEs) up to 25%, which is comparable to the best performance of OLEDs based on organic phosphorescent emitters [14]. Thus, TADF emitters are now regarded as the third generation of OLED emitters after fluorescent and phosphorescent emitters and will be the mainstream emitters of OLEDs. Both the improved stability and similar IQE of TADF emitters compared with that of phosphorescent emitters enable the potential application of TADF emitters in inverted OLEDs with high efficiency and excellent stability. However, no reports have been published on the construction and application of the inverted OLEDs based on TADF emitters, which inspired us to investigate the construction of high-efficiency inverted OLEDs based on TADF emitters. In 2014, our group reported on novel TADF emitters based on TX, and a high EQE of up to 21% was achieved for the OLEDs [15]. In this letter, we report the first inverted OLEDs based on TADF emitters. The devices consisted of an effective bottom cathode structure OLED with ZnO as the EIL and 2-pheyl-4'-carbazole-9-H-thioxanthen-9-one-10,10-dioxide (TXO-PhCz) as the TADF emitter, affording a maximum current efficiency of 28.1 cd A^{-1}, maximum power efficiency of 16.1 lm W^{-1}, and maximum EQE up to 9.8%.

The device structure of the inverted OLEDs and molecules and their energy levels are presented in Fig. 1. Efficient electron injection is an important issue in inverted OLEDs, because there is a large barrier between ITO and the electron transporting layer (ETL) due to the high work function of ITO up to 4.7–5.1 eV. ZnO films were used as the efficient and transparent EIL because of their wide band gap (E_g~3.5 eV), good electron transporting properties, and low work function. Moreover, ZnO films can be deposited using a solution-processed method at low temperature and exhibit excellent compatibility with plastic substrates, which is attractive for future plastic OLED displays with excellent flexibility. The devices were prepared as follows. Thin ZnO films were synthesized using a similar method to that described in previous reports and deposited onto pre-patterned ITO substrates using the spin-coating method [15]. Then, all the other layers, such as Cs_2CO_3, organic semiconducting layers, MoO_3, and Al, were deposited by sequential thermal evaporation under a base pressure of 4×10^{-4} Pa without breaking the vacuum. The structure of the inverted OLEDs was as follows: ITO/ZnO (x nm)/Cs_2CO_3 (y nm)/Alq3 (30 nm)/2,4,6-tris(biphenyl-3-yl)-1,3,5-triazine (T2T) (10 nm)/TXO-PhCz:mCBP (10% 30 nm)/1, 1-bis[(di-4-toly-

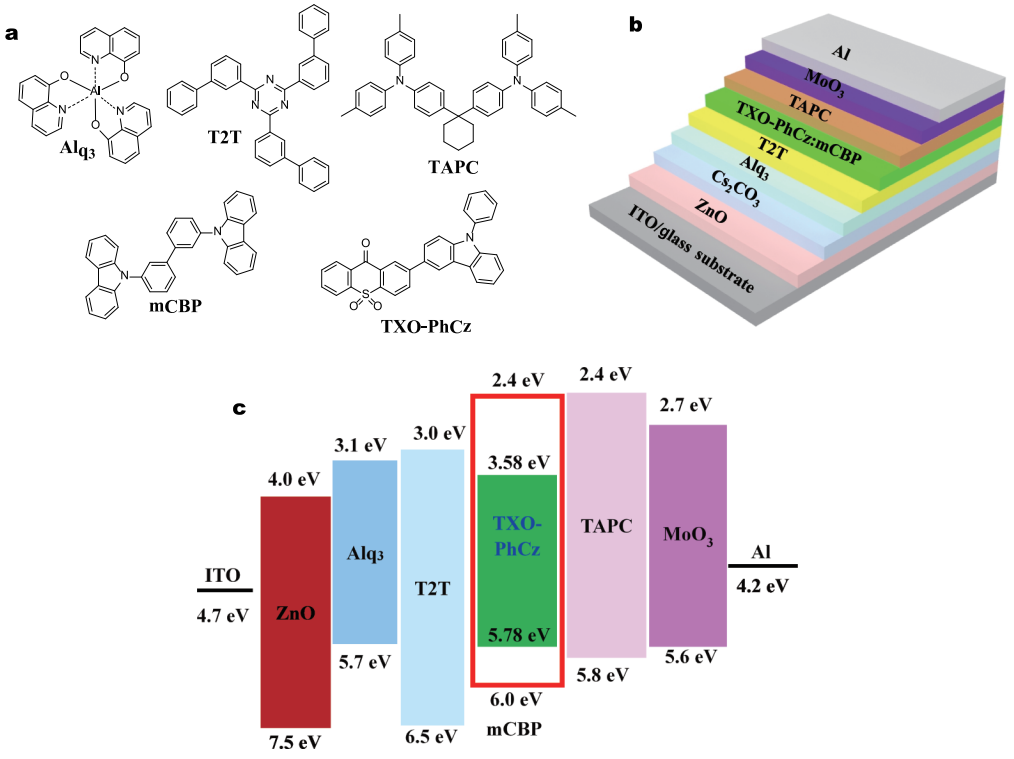

Figure 1 (a) Molecular structures of the organic semiconductors for the inverted OLEDs; (b) scheme of the inverted OLEDs; and (c) the energy levels of the materials involved in the inverted OLEDs.

lamino)phenyl]cyclohexane (TAPC) (50 nm)/MoO_3 (10 nm)/Al (100 nm) (x=40, 25, and 20 nm; y=0 and 7 nm). TAPC was used as the hole transporting layer (HTL), MoO_3 was used as the HIL, Alq3 was used as the ETL, Cs_2CO_3 was used as the EIL, and T2T was used as the hole blocking layer (HBL).

The surface of ZnO films must be smooth to prevent short circuits between the metal oxide and Al anode. Thus, the morphology of the ZnO layers with different thicknesses was investigated using atomic force microscopy (AFM). As observed in Fig. 2, the ITO surface is covered by ZnO films, and all the ZnO films are homogeneous and flat with a low roughness. The root-mean-square (RMS) roughnesses are 3.75, 3.30, and 2.26 nm for the ZnO films with thicknesses of 40, 25, and 20 nm, respectively. The RMS roughness decreases with increasing ZnO thickness. These roughness values are comparable and even lower than those of metal oxide films for inverted OLEDs, indicating that the ZnO films can be used for the EIL of OLEDs [16]. The transparencies of the ZnO films are also critical for the light out-coupling of OLEDs. The transparencies of ITO/ZnO films with different thicknesses are shown in Fig. 3. The transparency of the ITO/ZnO (20 nm) film is approximately 90% from 400 to 700 nm, which is comparable to that of ITO/glass substrates. Upon increasing the thickness of the ZnO film, there is a small decrease in the transparency of the ITO/ZnO films from 450 to 600 nm, and the transparency decreases from 90% of 20 nm to 87% of 40 nm at 500 nm. Almost no decrease of the transparency can be observed, and the transmission curves almost overlap. These results indicate that the ZnO films exhibit excellent transparency, and the thickness of ZnO films negligibly affects the light out-coupling of the inverted OLEDs, facilitating the fabrication of inverted OLEDs with high performance.

Fig. 4 shows the current density–voltage (J–V) and luminance–voltage (L–V) characteristics of the devices, in which a thin layer of Cs_2CO_3 was placed between the ZnO and Alq3 to enhance the electron injection from ZnO to the organic layer. The insertion of the thin Cs_2CO_3 layer can remarkably enhance the electron injection from ZnO [17], leading to a higher current density compared with that of the device without the thin Cs_2CO_3 layer. After the insertion of the thin Cs_2CO_3 layer, the thickness of the ZnO film cannot remarkably affect the current densities because of the high carrier mobility of ZnO films, leading to a similar current density for all the devices with different ZnO thicknesses. Similarly, the insertion of the thin ZnO layer can remarkably reduce the turn-on voltage of the devices. The devices with the 40-nm ZnO film can be turned on at

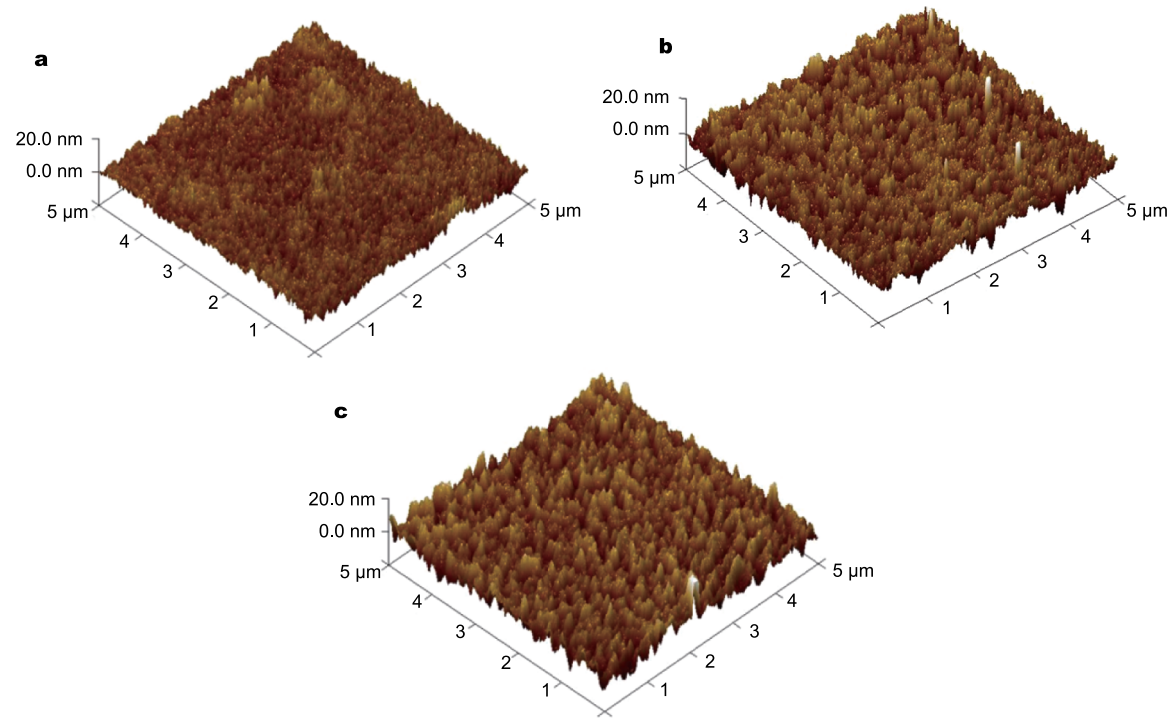

Figure 2 Three-dimensional topography of the surface of the ZnO films with different film thickness on ITO substrates: (a) 20; (b) 25; and (c) 40 nm. The image size are 5 μm×5 μm and the RMS roughness is approximately 3 nm.

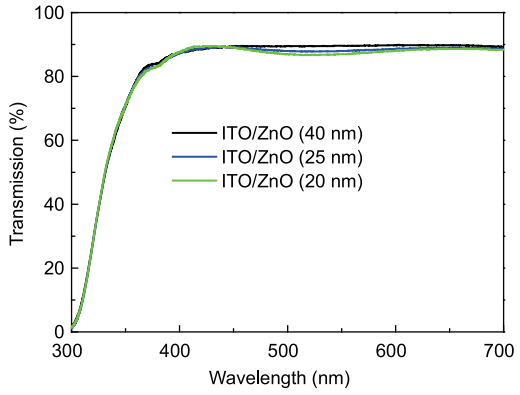

Figure 3 The transparencies of the ITO/ZnO films with different thickness (20, 25 and 40 nm).

7.25 V. The turn-on voltage was reduced to 6.25 V with the insertion of the 7-nm-thick Cs_2CO_3 layer. After the insertion of the thin Cs_2CO_3 layer, the lowest turn-on voltage of 4.9 V was obtained by the device with the ZnO film thickness of 25 nm. These results can be attributed to the optimized recombination zone in the emitting layer, as the excitons can leak into the neighbor layer because of the high triplet/singlet energy of mCBP. For the device with the 25-nm ZnO layer, the maximum luminance, L_{max}, was 8266 cd m^{-2} at 14.25 V, and the driving voltage for 1000 cd m^{-2} was only 11.5 V, which is much lower than the values of reported inverted OLEDs. These results indicate that the ZnO/Cs_2CO_3 layer can inject electrons very efficiently because of the improved energy-level matching. The turn-on voltages and driving voltages are still higher than those of phosphorescence OLEDs with optimal performance. These voltages can be further decreased by the development of new electron-injection materials from ZnO and organic layers [18]. Fig. 5 shows the light-emitting characteristics of the inverted OLEDs. A similar trend of turn-on voltages can also be observed for the device performance, including the current efficiency, power efficiency, and EQE. The devices without the 7-nm-thick Cs_2CO_3 layer emit green light with International Commission on Illumination (CIE) color coordinates of (0.35,0.57) and exhibit a current efficiency of 2.1 cd A^{-1}, a power efficiency of 0.6 lm W^{-1}, and an EQE of 0.7%. The performance of the device can be clearly enhanced with the insertion of a 7-nm-thick Cs_2CO_3 layer, affording a current efficiency of 6.2 cd A^{-1}, a power efficiency of 1.8 lm W^{-1}, and an EQE of 1.8%. The device with an optimized ZnO thickness of 25 nm exhibited the maximum performance, with a current efficiency of 28.1 cd A^{-1}, a power efficiency of 16.1 lm W^{-1}, and an EQE of 9.8%. This performance is among the best of those reported for OLEDs based on phosphorescent or fluorescent emitters [7,9,13]. Fig. 5d shows the electroluminescence (EL) of the devices. All the devices exhibited the typical EL spectrum of TXO-PhCz emission with CIE color coordinates of (0.35,0.57). It has been reported that the thickness of the ZnO layers can induce optical interference effects, leading to the change in the spectra characteristics of the EL emission [16]. However, the EL spectra of all the devices overlapped, demonstrating the excellent transparency of the ZnO film. These findings coincide with the results above, demonstrating the excellent properties and potential application for the EIL for inverted OLEDs. To the best of our knowledge, these inverted OLEDs are the first to be based on the TADF emitter.

In summary, for the first time, we have demonstrated efficient green inverted OLEDs based on a TADF emitter, TXO-PhCz, with a transparent ITO/ZnO cathode. The device with a 25-nm ZnO film and 7-nm Cs_2CO_3 layer can be turned on at 4.9 V with maximum efficiencies of 28.1 cd A^{-1}, 16.1 lm W^{-1}, and 9.8%. The thin Cs_2CO_3 layer can

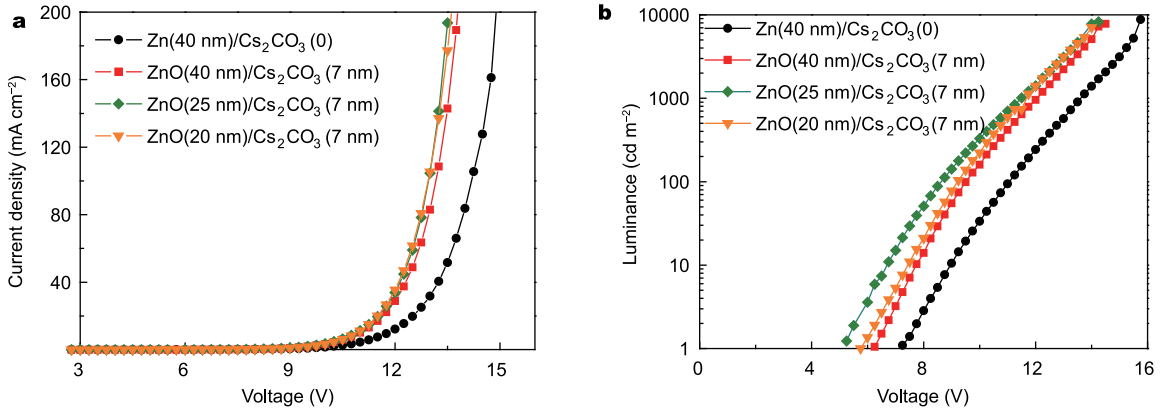

Figure 4 (a) The *J*–*V*; (b) *L*–*V* characteristics of the devices fabricated with different ZnO layer thicknesses.

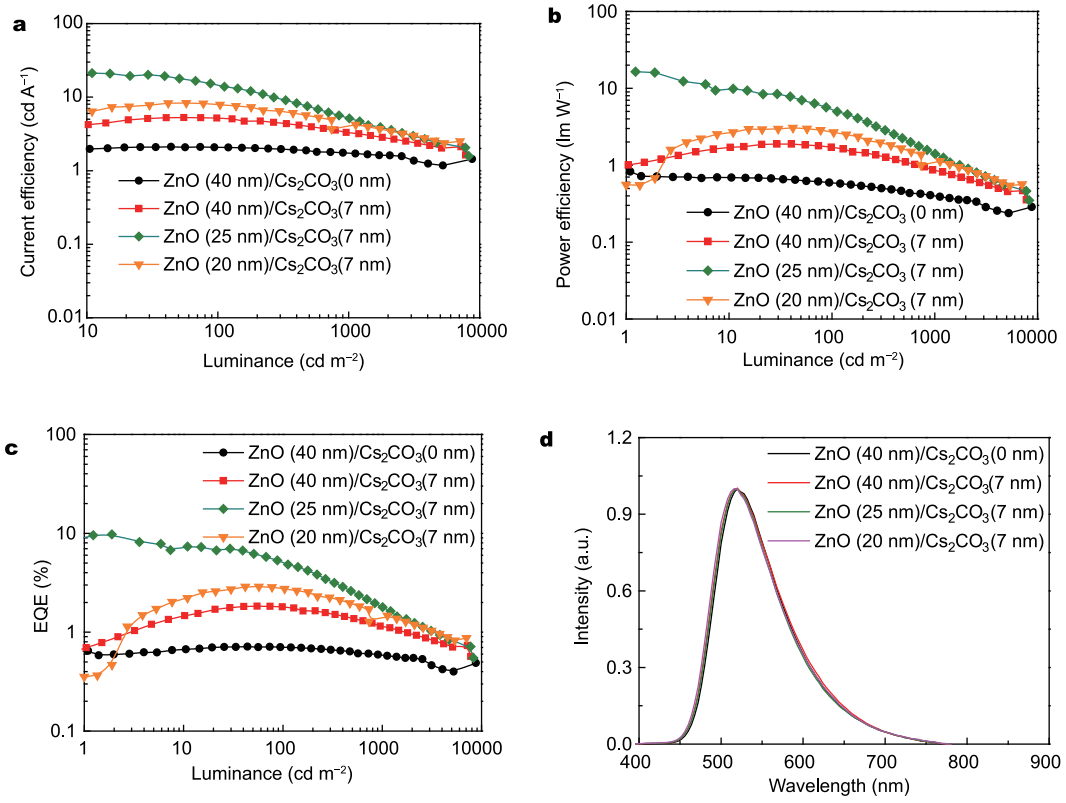

Figure 5 (a) The current efficiency-luminance characteristics; (b) the power efficiency-luminance characteristics; (c) EQE-luminance characteristics of the inverted OLEDs with different ZnO thicknesses. (d) Normalized EL spectra of the inverted OLEDs with different ZnO thicknesses at the same voltage of 8 V.

form a thin interfacial EIL and HBL. These results demonstrate that the inverted OLEDs based on TADF emitters can be competitive compared with conventional OLEDs because of their air-stable electrodes and TADF emitters, which enable simpler encapsulation, paving new avenues for increasing the use of air-stable OLEDs with high performance.

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Author contributions Lv X and Wang Y designed the project, and the experiments. Lv X performed the experiments, and Lv X wrote the paper with support from Wang Y. All authors contributed to the general discussion.

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

Supplementary information Supplementary data are available in the online version of the paper.

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基于热激活延迟荧光材料的高效倒向有机发光二极管

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摘要 本论文首次报道了基于热激活延迟荧光材料TXO-PhCz的倒置结构绿光有机电致发光器件. 器件以ITO/ZnO作为电子注入阴极, 提高了电子向Alq3层中的有效注入. 7 nm 的Cs_2CO_3可以进一步提高电子的注入效率. 最优化器件以25-nm ZnO和7-nm Cs_2CO_3层实现了电子的有效注入, 器件显示出最佳性能, 器件的电流效率为28.1 cd A^{-1}, 功率为16.1 lm W^{-1}, 外量子效率达9.8%. 基于TADF发光材料的倒向OLEDs器件由于其电极材料和发光材料的优异稳定性, 可以实现简单封装, 有望替代传统OLEDs.