Letter

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Enhanced efficiency of all-inorganic perovskite light-emitting diodes by using F4-TCNQ-doped PTAA as a hole-transport layer

Yu-Shan Liu,¹ Shuang Guo,¹ Jing Feng,^{1,3} Yue-Feng Liu,¹ Yan-Gang Bi,¹ Da Yin,¹ Xu-Lin Zhang,¹ and Hong-Bo Sun^{1,2,4}

¹State Key Laboratory of Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, Changchun 130012, China ²State Key Laboratory of Precision Measurement Technology and Instruments, Department of Precision Instrument, Tsinghua University, Haidian, Beijing 100084, China ³e-mail: jingfeng@jlu.edu.cn

⁴e-mail: hbsun@tsinghua.edu.cn

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We demonstrate an enhanced efficiency of all-inorganic perovskite light-emitting diodes (PeLEDs) by doping an electron acceptor of 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ) as a p-type dopant into the hole-transport layer (HTL) of poly-triarylamine (PTAA). The conductivity of the PTAA was improved by the formation of the CT complex through the electron transfer from the PTAA to F4TCNQ. Moreover, the hydrophobic surface of the PTAA leads to an improved surface morphology of the perovskite films compared to that on the conventionally used HTL of PEDOT:PSS. As a result, the maximum luminance and efficiency for the doped PTAA-based PeLEDs are 28020 cd/m² and 13.5 cd/A, respectively, corresponding to 32.7% and 48% improvement in the efficiency compared to those of the pure PTAA or PEDOT: PSS-based PeLEDs. © 2019 Optical Society of America

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Recently, solution-processed perovskites have demonstrated huge potential for the next generation of low-cost, high-quality optoelectronic devices, such as solar cells, photodetectors, and light-emitting diodes [1–8]. Compared with traditional lightemitting materials, perovskite has many advantages [9,10]. Electroluminescence (EL) from perovskite light-emitting diodes (PeLEDs) was first reported in 2014 [3]. By a nanocrystal pinning process and a method of spin-coating stoichiometrically modified perovskite solutions, the current efficiency (CE) of organic-inorganic hybrid PeLEDs has been boosted to 42.9 cd/A [11]. Compared with the organic-inorganic hybrid perovskites (e.g., MAPbBr3), all-inorganic perovskite emitters (e.g., CsPbBr3) have shown great photoluminescence (PL) quantum yields [12-14], tunable bandgaps, and high color purity. More importantly, all-inorganic perovskites have attracted favorable attention due to their thermal and moisture stability, motivating applications in lighting, flat-panel displays, and laser projection displays [15]. The performance of all-inorganic perovskite-based PeLEDs has recently surpassed that of hybrid PeLEDs. You et al. successfully obtained PeLEDs with a brightness of over 91000 cd/m^2 which is the world record up to now [16]. In order to further improve the efficiency of the PeLEDs, much work has focused on the development of charge transport materials [17–21]. Most of the hole-transport materials (HTMs) valid in organic lightemitting diodes (OLEDs) [22,23] cannot be employed in PeLEDs, because the solvents utilized for perovskite solutions, such as N,N-dimethylformamide (DMF) or dimethyl sulfoxide, can wash off the organic HTMs. Therefore, poly(3,4ethylenedio-xythiophene):poly(styrenesulfonate) (PEDOT:PSS) is regarded as the most used hole-transport layer (HTL) [3,24]. However, PEDOT:PSS introduced between the indium tin oxide (ITO) anode and perovskite film would etch the underlying ITO due to its acidic nature [25], which limits the EL performance and long-term stability of the PeLEDs.

Recently, poly-triarylamine (PTAA) has attracted much attention as an HTL in perovskite solar cells, because the perovskite films can form a better surface morphology on the nonwetting surface of the PTAA [26,27]. Inspired by the successful application of the PTAA in the perovskite solar cells, it is possible to employ the PTAA in all-inorganic PeLEDs as the HTL to improve the surface morphology of perovskite films. However, the low conductivity of the PTAA is a limitation for the high performance of PeLEDs. P-type doping has been widely used in OLEDs to generate holes in the HTL by doping an electron acceptor in the HTL to facilitate the conductivity of the HTL. Among the various kinds of p-type dopants in the OLEDs, 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ) has been demonstrated as a very strong electron acceptor to improve the hole injection and transport in the OLEDs. Therefore, we can expect to enhance the conductivity of the PTAA by using the p-type dopant.

In this Letter, F4-TCNQ has been employed as the p-type dopant in the PTAA, and enhanced EL performance of the PeLEDs based on the HTL of the doped PTAA has been obtained. The highest occupied molecular orbital (HOMO) level of the PTAA is close to the lowest unoccupied molecular orbital (LUMO) level of F4-TCNQ, and a p-type doping process occurred as the electron transfer from the HOMO level of the PTAA to the LUMO level of F4-TCNQ. The hole transport can be enhanced by p-type doping, which has been confirmed by a much improved current density of the hole-only device with the F4-TCNQ-doped PTAA. The doped PTAA-based PeLEDs exhibit the maximum luminance and efficiency of 28020 cd/m² and 13.5 cd/A, respectively. Finally, 32.7% and 48% improvements in the efficiency are achieved compared to that of the pure PTAA or PEDOT:PSS-based PeLEDs, respectively.

Figures 1(a)-1(c) show the SEM images of the perovskite films deposited on PEDOT:PSS, pure PTAA, or F4-TCNQdoped PTAA films on ITO/glass substrate, respectively. The perovskite film on PEDOT:PSS exhibits numerous pin-hole defects [Fig. 1(a)], which may lead to leakage current in the PeLEDs, thereby decreasing the device performance. We can see that the morphology of the perovskite films was remarkably improved with much less pin-hole defects when deposited on the F4-TCNQ-doped PTAA [Fig. 1(c)] layer compared with those on PEDOT:PSS [Fig. 1(a)]. According to Figs. 1(b) and 1(c), the perovskite films exhibited no obvious difference while deposited on the pure or F4-TNCQ-doped PTAA, indicating that the F4-TCNQ dopant has negligible influence on the morphology of the perovskite films.

Figure 1(d) presents the cross-sectional SEM image of the PeLEDs. Considering the hydrophobic property of the PTAA surface, we introduced a DMF-assist method in the spin-coating process of the perovskite solution to ensure that the perovskite solutions can be successfully spin-coated on the F4-TCNQ-doped PTAA layer. The device structure is ITO (200 nm)/ HTL (30 nm)/CsPbBr3 (60 nm)/LiF (0.5 nm)/Al (120 nm). The DMF infiltrates the surface of the substrates, thereby facilitating the perovskite precursor solution to spread on the substrates and forming uniform films.



Fig. 1. SEM images of the perovskite films deposited on the (a) PEDOT:PSS, (b) pure PTAA, and (c) F4-TCNQ-doped PTAA films. (d) Cross-sectional image of the PeLEDs.

The crystallization quality of the perovskite film on pure PTAA, doped PTAA, and PEDOT:PSS films is further investigated through PL and x-ray diffraction (XRD) measurements [Figs. 2(a) and 2(b). As shown in Fig. 2(a), the perovskite films deposited on the pure PTAA and doped PTAA exhibited an obvious enhancement in PL intensity compared to the perovskite film on PEDOT:PSS. This result testifies that the nonradiative recombination at the interface between the perovskite and HTL has been suppressed because of the better morphology of the perovskite films on the PTAA film. The XRD pattern of perovskite films deposited on the pure PTAA, doped PTAA, and PEDOT:PSS substrates are shown in Fig. 2(b). It can be seen that no obvious impure peak is observed, while the intensity of characteristic peaks of perovskite on the pure PTAA and doped PTAA is higher than that on PEDOT:PSS substrates, indicating that better quality of crystallization of perovskite films is formed on the pure PTAA and doped PTAA films.

It has been demonstrated that *p*-type dopants form charge transfer (CT) complexes with the hole-transport molecules by the electron transfer from the hole-transport molecules to the p-dopants. The formation of the CT complex can be easily confirmed by the appearance of additional peaks in the NIR region. Figure 3(a) shows the absorption spectra of the F4-TCNQ, PTAA, and F4-TCNQ-doped PTAA in chlorobenzene. The pure PTAA and F4-TCNQ exhibit the absorption peak maximum at 390 and 387 nm, respectively. There is no absorption above 500 nm for both the pure PTAA and F4-TCNQ. After mixing the PTAA and F4-TCNQ, a new absorption peak appears at 780 nm, indicating the formation of the CT complex [26,28–30]. The HOMO level of the PTAA (5.14 eV) is close



Fig. 2. (a) PL intensity and (b) XRD pattern of the perovskite films on different HTLs.



Fig. 3. (a) Absorption spectra of the F4-TCNQ, PTAA, and F4-TCNQ-doped PTAA in chlorobenzene. (b) J-V curves of hole-only devices with the pristine PTAA and F4-TCNQ-doped PTAA.

to the LUMO level of the F4-TCNQ (5.24 eV) [26], resulting in the electron transfer from the PTAA HOMO to the F4-TCNQ LUMO. A large number of additional holes in the PTAA induced by the electron transfer improve its hole transport [26,31]. The effect of doping on the hole transport was investigated by comparing the hole-only devices with different HTLs. The device structure is ITO/HTL/Au. As shown in Fig. 3(b), the current density of the hole-only device using the p-doped HTL is obviously higher than that of the hole-only device with the pure PTAA. Thus, an effective improvement of the hole transport is achieved after doping the F4-TCNQ into the PTAA.

The EL performance of the doped PTAA-based PeLEDs with different doping concentrations of the F4-TCNQ, as well as the reference device with PEDOT:PSS HTL, has been compared and summarized in Fig. 4. The current density of the doped PTAA-based PeLEDs is slightly higher than that of the pure-PTAA-based devices due to the improved hole transport induced by the dopant [Fig. 4(a)]. Both the luminance [Fig. 4(b)] and CE [Fig. 4(c)] of the PeLEDs reach a maximum value at the doping ratio of 5%, which is 28020 cd/m^2 and 14.3 cd/A, respectively. The efficiency is 32.7% higher than that of the device using the pure PTAA HTL (10.78 cd/A). The maximum efficiency of the doped PTAA device is increased by 48% compared to the PEDOT:PSS-based device (9.1 cd/A). It can be seen that the PeLEDs using different HTLs exhibited no obvious change in EL spectra, and the peaks are all located at 512 nm [Fig. 4(d)]. This indicates that the crystal structure and optical properties of the perovskite film are not affected by the various HTLs. The inset in the Fig. 4(d)shows the photograph of the PeLED working at 5 V using a F4-TCNQ-doped HTL in the air, and no cracks and dark spots can be observed.

In summary, we have demonstrated the improved efficiency of PeLEDs with the p-doped PTAA as the HTL. The conductivity of the PTAA was enhanced by the formation of a CT complex through the electron transfer from the PTAA to



Fig. 4. EL performance of PeLEDs devices with the F4-TCNQdoped PTAA HTLs at different doping concentrations and PEDOT:PSS HTLs. (a) Current density-voltage, (b) luminancevoltage, (c) and CE-voltage curves; (d) EL spectrum. The inset in (d) is a photograph of the operating device at a driving voltage of 5 V.

F4-TCNQ. On the other hand, the perovskite films deposited on the PTAA HTL exhibit better surface morphology compared to that on the PEDOT:PSS HTL, which also contributed to the improved performance of the PeLEDs. The maximum efficiency of the PeLEDs with the p-doped PTAA HTL is 32.7% and 48% higher than that of the device with the pure PTAA or PEDOT:PSS HTL, respectively. Therefore, the F4-TCNQ-doped PTAA HTL can greatly improve the performance of the PeLEDs, thus having good application prospects in the future commercial application of large-area perovskite illumination and flat panel display.

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