Highly Efficient Green InP Quantum Dot Light-Emitting Diodes by Enhancing Carrier Injection

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ABSTRACT

Enhancing carrier injection is essential to indium phosphide (InP) quantum dot light-emitting diodes (QLEDs). Here, an electric dipole layer is introduced to enhance the hole injection in the green InP QLED with a highly mobility electron transport layer (ETL). The optimized green InP QLED had achieved a 1.7 times EQE enhancement.

1 Introduction

Quantum dot light-emitting diodes (QLEDs) have emerged in display application for their extraordinary merits, including tunable spectrum, high color saturation, low energy consumption, and low-cost solution processability [1-5]. However, the environmental contamination limits the further applications of Cd-based QLEDs [6, 7] thus many environmental-friendly alternatives have been explored urgently [8-15]. Among them, indium phosphide (InP)-based quantum dots (QDs) are considered as one of the best candidates for commercial display applications [16-18]. With the advancement of material synthesis, the photoluminescence quantum yield (PLQY) of green InP QDs (>95%) has caught up with the level of Cd-based QDs [16], but the inferior carrier injection problem has still lagged the performance of green InP QLEDs [19-22].

In working green InP QLEDs, part of the holes will be accumulated at the interface of hole injection layer (HIL) and hole transport layer (HTL) inevitably due to the energy barrier. Meanwhile, the hole injection is also impeded because of the energy-level offset between green InP QDs and HTL [2, 23, 24]. Different from the hole injection, the electron is usually over injection in the green InP QLEDs due to the high electron mobility of the electron transport layer (ETL) [25-29]. Therefore, carriers in green InP QLEDs are more imbalanced, resulting a poor efficiency in the green InP QLEDs.

In this work, we have compared the green InP QLEDs with the ETL of ZnO and ZnMgO by simulation and find that green InP QLEDs based on ZnO ETL will have a higher recombination rate. The higher electron mobility of ZnO makes a strengthened electron injection in the device. To enhance the hole injection, we have introduced an ultra-thin MoO_3 electric dipole layer between the HIL and HTL. Compared with the contrast device, a 1.7 times EQE enhancement from 4.25% to 7.39% is achieved. This work has provided an effective approach to enhance carrier injection in green InP QLEDs and indicates the feasibility to realize highly efficient green InP QLEDs.

2 Experiment

The electrical simulations were performed with Setfos 4.6 software, while the constant or field-dependent electron and hole mobilities according to the Poole–Frenkel model were used in the simulations. The boundary conditions for the charge carrier densities at the electrodes were set to satisfy the Fermi-level alignment at thermal equilibrium. Exciton generation is permitted only in the emission layer and follows the standard Langevin recombination.

The contrast QLED devices were fabricated with structure of ITO/PEDOT: PSS/PVK/QDs/ZnMgO or ZnO/Al. The patterned ITO electrodes were cleaned and treated with plasma before use. All the function layers except MoO_3 nor LiF were deposited via spin-coating at 3000 rpm for 45 s with the assistance of thermal annealing. MoO_3, LiF and Al electrodes were deposited by thermal evaporation under a vacuum of 5×10^{-4} Pa.

The luminance area of our devices was 2×2 mm^2. The PLQY and PL spectra were measured with the excitation wavelength of 365 nm by absolute PLQY spectrometer. The devices were assumed as a lambert illuminant, and the current density–voltage–luminance (*J-V-L*) curves were measured by a Keithley 2614B source and a PIN–25D silicon photodiode. All measurements were performed at room temperature.

3 Results and Discussion

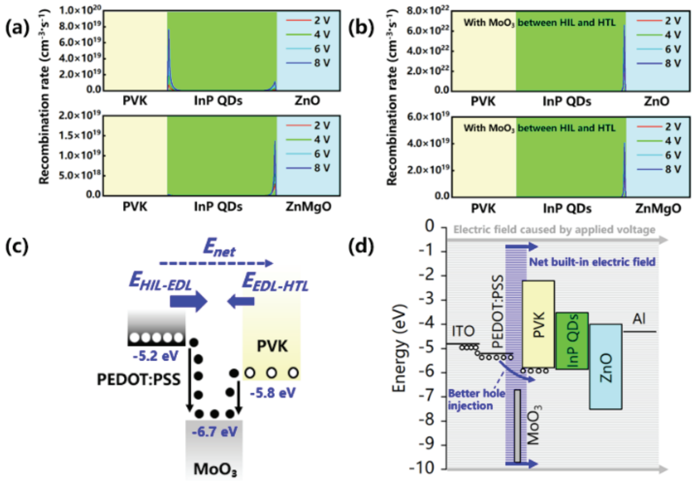

Fig. 1 (a)& (b) Distribution of recombination rate in the green InP QLED without/with MoO_3. (c) Schematic of carrier transfer. (d) Schematic of holes transfer in PEDOT: PSS/MoO_3/PVK interfaces in green InP QLED.

We have established carrier recombination models according to actual green InP QLEDs. Fig. 1(a)&(b) shows the distribution of the recombination rate at different bias voltage in the green InP QLEDs based on two different ETLs (ZnO and ZnMgO). The recombination peaks in the ZnO-based device are higher than which in the ZnMgO-based device. Meanwhile, an ultra-thin MoO_3 layer is inserted at the interface of PEDOT: PSS and PVK. Owing to the larger energy level difference between PEDOT: PSS and MoO_3 (1.5 eV) compared with which of MoO_3 and PVK (0.9 eV) (Fig. 1(c)), a positive net electric field (E_{net}) is in the same direction of the electric field driven by the applied forward voltage as shown in Fig. 1(d). The simulation result illustrates that the inserting of MoO_3 layer has strengthened the hole injection in green InP QLEDs, hence the recombination rate enhanced dramatically.

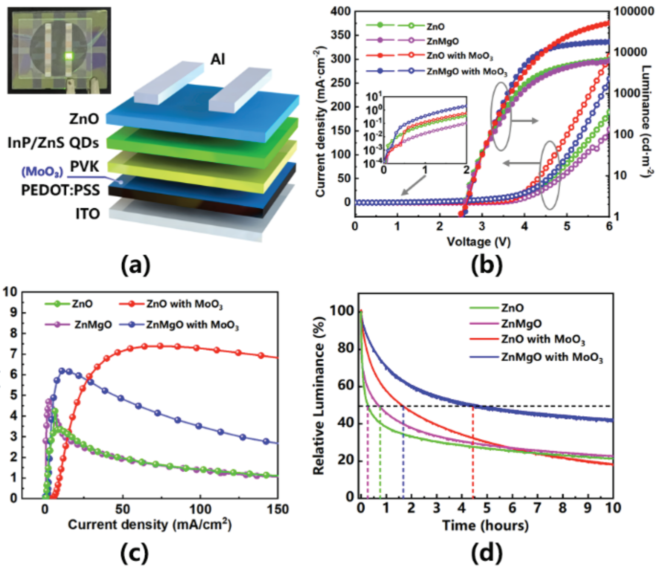

Fig. 2 (a) Device structure of typical green InP QLEDs with MoO_3 interlayer. Inset: photographs of the operating device. (b) *J−V−L* characteristics. Inset: *J−V* characteristics in log scale in low-voltage region, (c) EQE versus J and (d) lifetime with the initial luminance of 1000 cd·m^{-2}.

Green InP QLEDs were fabricated and characterized to demonstrate the balance of carrier injection. Consequently, the maximum luminance of green InP QLED is enhanced from 6482 to 6794 (applying ZnO ETL) and then 52,730 cd·m^{-2} (inserting MoO_3 interlayer), which is an 8.1 times improvement overall. As demonstrated in Fig. 2(d), the EQE of the ZnO-based green InP QLEDs increased from 4.25% to 7.39% and the ZnMgO-based one increased from 4.69% to 6.19%. The low EQE of ZnO-based contrast device indicates that the excess electron injection leads more non-radiative recombination. However, the larger EQE enhancements of ZnO-based device confirms that a higher recombination rate and good carrier balance have been achieved by the ZnO ETL and MoO_3 interlayer. Meanwhile, the damage of accumulated holes at the PEDOT:PSS/PVK interface was reduced obviously because the hole hopping was enhanced by the MoO_3. As a result, the phenomenon of efficiency roll-off had been finally relieved. The ZnO-based green InP QLED with the MoO_3 exhibited longer lifetime, and its T_{50} at 100 cd·m^{-2} is predicted to be 104.09 h, using the acceleration factor of 1.8 (given that we measured the real lifetime at 1,000 cd·m^{-2}), compared to the contrast device (T_{50} = 15.77 h) (Fig. 2(d)).

4 Conclusions

In summary, we have introduced a MoO_3 electric dipole layer to enhance the hole injection in green InP QLEDs with ZnO ETL. This approach can effectively improve the recombination rate in green InP QLEDs and achieve highly efficient devices. Benefit from the strengthened carrier injection, green InP QLED had achieved EQE as 7.39%, which has a 1.7 times enhancement, indicating a feasible approach to promote a green InP QLED performance.

References

[1] V. L. Colvin, M. C. Schlamp, and A. P. Alivisatos, "Light-emitting diodes made from cadmium selenide nanocrystals and a semiconducting polymer," Nature, Vol. 370, No. 6488, pp. 354-357 (1994).

[2] X. L. Dai, Z. X. Zhang, Y. Z. Jin, Y. Niu, H. J. Cao, X. Y. Liang, L. W. Chen, J. P. Wang, and X. G. Peng, "Solution-processed, high-performance light-emitting diodes based on quantum dots," Nature, Vol. 515, No. 7525, pp. 96-99 (2014).

[3] J. J. Hao, H. C. Liu, J. Miao, R. Lu, Z. M. Zhou, B. X. Zhao, B. Xie, J. J. Cheng, K. Wang, and M. H.

Delville, "A facile route to synthesize CdSe/ZnS thick-shell quantum dots with precisely controlled green emission properties: towards QDs based LED applications," Sci. Rep., Vol. 9, No. 1, pp. 12048 (2019).

[4] W. R. Cao, C. Y. Xiang, Y. X. Yang, Q. Chen, L. W. Chen, X. L. Yan, and L. Qian, "Highly stable QLEDs with improved hole injection via quantum dot structure tailoring," Nat. Commun., Vol. 9, No. 1, pp. 2608 (2018).

[5] H. C. Liu, H. Y. Zhong, F. K. Zheng, Y. Xie, D. P. Li, D. Wu, Z. M. Zhou, X.-W. Sun, and K. Wang, "Near-infrared lead chalcogenide quantum dots: Synthesis and applications in light emitting diodes," Chin. Phys. B, Vol. 28, No. 12, pp. 128504 (2019).

[6] L. N. Kolonel, "Association of cadmium with renal cancer," Cancer, Vol. 37, No. 4, pp. 1782-1787 (1976).

[7] L. Järup, "Hazards of heavy metal contamination," Br. Med. Bull., Vol. 68, No. 1, pp. 167-182 (2003).

[8] A. A. Guzelian, J. E. B. Katari, A. V. Kadavanich, U. Banin, K. Hamad, E. Juban, A. P. Alivisatos, R. H. Wolters, C. C. Arnold, and J. R. Heath, "Synthesis of Size-Selected, Surface-Passivated InP Nanocrystals," J. Phys. Chem., Vol. 100, No. 17, pp. 7212-7219 (1996).

[9] O. I. Mićić, H. M. Cheong, H. Fu, A. Zunger, J. R. Sprague, A. Mascarenhas, and A. J. Nozik, "Size-Dependent Spectroscopy of InP Quantum Dots," J. Phy. Chem. B, Vol. 101, No. 25, pp. 4904-4912 (1997).

[10] A. Q. Wang, H. B. Shen, S. P. Zang, Q. L. Lin, H. Z. Wang, L. Qian, J. Z. Niu, and L. S. Li, "Bright, efficient, and color-stable violet ZnSe-based quantum dot light-emitting diodes," Nanoscale, Vol. 7, No. 7, pp. 2951-2959 (2015).

[11] C. Y. Xiang, W. Koo, S. Chen, F. So, X. Liu, X. X. Kong, and Y. J. Wang, "Solution processed multilayer cadmium-free blue/violet emitting quantum dots light emitting diodes," Appl. Phys. Lett., Vol. 101, No. 5, pp. (2012).

[12] X. Huang, R. M. Yu, X. Q. Yang, X. M. Xu, H. Zhang, and D. D. Zhang, "Efficient CuInS2/ZnS based quantum dot light emitting diodes by engineering the exciton formation interface," J. Lumin, Vol. 202, pp. 339-344 (2018).

[13] L. Li, A. Pandey, D. J. Werder, B. P. Khanal, J. M. Pietryga, and V. I. Klimov, "Efficient Synthesis of Highly Luminescent Copper Indium Sulfide-Based Core/Shell Nanocrystals with Surprisingly Long-Lived Emission," J. Am. Chem. Soc., Vol. 133, No. 5, pp.1176-1179 (2011).

[14] F. Wang, Y. H. Chen, C. Y. Liu, and D. G. Ma, "White light-emitting devices based on carbon dots' electroluminescence," Chem. Commun., Vol. 47, No. 12, pp. 3502-4 (2011).

[15] B. H. Kim, C. H. Cho, J. S. Mun, M. K. Kwon, T. Y. Park, J. S. Kim, C. C. Byeon, J. M. Lee, and S. J. Park, "Enhancement of the External Quantum Efficiency of a Silicon Quantum Dot Light-Emitting Diode by Localized Surface Plasmons," Adv. Mater., Vol. 20, No. 16, pp. 3100-3104 (2008).

[16] P. Liu, Y. J. Lou, S. H. Ding, W. D. Zhang, Z. H. Wu, H. C. Yang, B. Xu, K. Wang, and X. W. Sun, "Green InP/ZnSeS/ZnS Core Multi‐Shelled Quantum Dots Synthesized with Aminophosphine for Effective Display Applications," Adv. Funct. Mater, Vol. 31, No. 11 (2021).

[17] D. Battaglia and X. G. Peng, "Formation of High Quality InP and InAs Nanocrystals in a Noncoordinating Solvent," Nano Lett., Vol. 2, No. 9, pp. 1027-1030 (2002).

[18] L. Li and P. Reiss, "One-pot Synthesis of Highly Luminescent InP/ZnS Nanocrystals without Precursor Injection," J. Am. Chem. Soc., Vol. 130, No. 35, pp. 11588-11589 (2008).

[19] H. Moon, W. Lee, J. Kim, D. Lee, S. Cha, S. Shin, and H. Chae, "Composition-tailored ZnMgO nanoparticles for electron transport layers of highly efficient and bright InP-based quantum dot light emitting diodes," Chem. Commun., Vol. 55, No. 88, pp. 13299-13302 (2019).

[20] S. H. Guo, Q. Q. Wu, L. Wang, F. Cao, Y. J. Dou, Y. M. Wang, Z. J. Sun, C. X. Zhang, and X. Y. Yang, "Boosting Efficiency of InP Quantum Dots-Based Light-Emitting Diodes by an In-Doped ZnO Electron Transport Layer," IEEE Electron Device Lett., Vol. 42, No. 12, pp. 1806-1809 (2021).

[21] W. C. Chao, T. H. Chiang, Y. C. Liu, Z. X. Huang, C. C. Liao, C. H. Chu, C. H. Wang, H. W. Tseng, W. Y. Hung, and P. T. Chou, "High efficiency green InP quantum dot light-emitting diodes by balancing electron and hole mobility," Commun. Mater., Vol. 2, No. 1, (2021).

[22] Q. Su, H. Zhang, and S. M. Chen, "Identification of excess charge carriers in InP-based quantum-dot light-emitting diodes," Appl. Phys. Lett., Vol. 117, No. 5, (2020).

[23] B. S. Mashford, M. Stevenson, Z. Popovic, C. Hamilton, Z. Q. Zhou, C. Breen, J. Steckel, V. Bulovic, M. Bawendi, S. Coe-Sullivan, and P. T. Kazlas, "High-efficiency quantum-dot light-emitting devices with enhanced charge injection," Nat. Photonics, Vol. 7, No. 5, pp. 407-412 (2013).

[24] Y. X. Yang, Y. Zheng, W. R. Cao, A. Titov, J. Hyvonen, J. R. Manders, J. Xue, P. H. Holloway, and L. Qian, "High-efficiency light-emitting devices based on quantum dots with tailored nanostructures," Nat. Photonics, Vol. 9, No. 4, pp. 259-266 (2015).

[25] H. C. Wang, H. Zhang, H. Y. Chen, H. C. Yeh, M. R. Tseng, R. J. Chung, S. M. Chen, and R. S. Liu, "Cadmium-Free InP/ZnSeS/ZnS Heterostructure-Based Quantum Dot Light-Emitting Diodes with a ZnMgO Electron Transport Layer and a Brightness of Over 10 000 cd m−2," Small, Vol. 13, No. 13, (2017).
[26] T. Lee, D. Hahm, K. Kim, W. K. Bae, C. Lee, and J. Kwak, "Highly Efficient and Bright Inverted Top ‐ Emitting InP Quantum Dot Light ‐ Emitting Diodes Introducing a Hole ‐ Suppressing Interlayer," Small, Vol.15, No. 50, pp. 1905162 (2019).
[27] D. Hahm, J. H. Chang, B. G. Jeong, P. Park, J. Kim, S. Lee, J. Choi, W. D. Kim, S. Rhee, J. Lim, D. C. Lee, C. Lee, K. Char, and W. K. Bae, "Design Principle for Bright, Robust, and Color-Pure InP/ZnSexS1–x/ZnS Heterostructures," Chem. Mater., Vol. 31, No. 9, pp.-3484 (2019).
[28] G. Motomura, K. Ogura, Y. Iwasaki, J. Nagakubo, M. Hirakawa, T. Nishihashi, and T. Tsuzuki, "Improvement of electroluminescent characteristics in quantum dot light-emitting diodes using ZnInP/ZnSe/ZnS quantum dots by mixing an electron transport material into the light-emitting layer," AIP Adv., Vol. 10, No. 6, (2020).
[29] Y. Iwasaki, G. Motomura, K. Ogura, and T. Tsuzuki, "Efficient green InP quantum dot light-emitting diodes using suitable organic electron-transporting materials," Appl. Phys. Lett., Vol. 117, No. 11, (2020).