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InP/ZnSe/ZnS/ZnS Blue Quantum Dots for Efficient Light-Emitting Diodes

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ABSTRACT

In this work, efficient pure blue InP/ZnSe/ZnS/ZnS QDs with emission wavelength of 470 nm are synthesized by optimizing the thick shell structure. Residual zinc stearate coated on QDs is removed successfully which facilitates the injection of holes. External quantum efficiency can reach to 1.7% for pure blue InP QLED.

1 INTRODUCTION

Quantum dots (QDs) is a kind of zero-dimensional semiconductor material, whose colors can be tuned by controlling their sizes. At present, cadmium (Cd) -based QDs have been commercialized in the field of backlight display.[1] However, due to the biological toxicity of Cd, applications of Cd-based QDs are limited. Although perovskite QDs have nearly a 100% QY, their stability seems an intrinsic weakness for electroluminescent applications.[2] III-V group InP QDs have stable structure and excellent properties, which is a promising candidate for displays. At present, the performance of green and red InP QDs materials and QLED devices have been significantly improved. In 2019, Shen et al [3] prepared green InP QDs. The external quantum efficiency (EQE) and current efficiency (CE) of green InP QLED were 6.3% and 13.7 Cd/A, respectively. Jang et al [4] improved the performance of red InP QDs by adding hydrofluoric acid to etch the oxidative core and optimized shell thickness to suppresses energy transfer. The EQE of QLED was 21.4%, and the maximum luminance was more than 100000 cd/m^2. However, there were few reports on blue-emitting InP QDs materials and devices. In 2020, Du et al [5] reported the synthesis of InP/GaP/ZnS QDs with size of 7.0 ± 0.9 nm. The emission wavelength of QLEDs was 488 nm and EQE reached to 1.01%.

In this work, pure blue InP QDs were synthesized with emission wavelength of 470 nm, quantum yield (QY) of 65%, and FWHM of 47 nm. Since the zinc stearate added during coating the ZnS shell is excessive, a small amount of zinc stearate remains on the QDs after purification, which impedes carrier injection in QLED. In order to solve this problem and at the same time to increase the shell thickness of InP QDs and reduce the energy transfer between QDs, we added S-TOP and $Zn(OA)_2$ to continue coating ZnS shell, and the excessive S-TOP will also react with and remove the residual zinc stearate. After reaction, the shell thickness was increased by 1.5 nm, and the thick shell InP/ZnSe/ZnS/ZnS QDs were more stable than the thin shell InP/ZnSe/ZnS QDs. At the same time, EQE increased from 0.6% in InP/ZnSe/ZnS QLED to 1.7% in InP/ZnSe/ZnS/ZnS QLED due to the increased hole injection efficiency of the device.

2 EXPERIMENT

0.34 mmol InI_3, 2.2 mmol ZnI_2, and 5 ml OLA were added into three-necked bottle. The mixture was degassed to remove water and oxygen. Then the reaction was flooded with Ar and further heated to 200 °C. 0.45 ml (2.4 mmol) $(DMA)_3P$ mixed with 1 ml OLA was injected into the reaction solution quickly and reaction 20 min. Then injection 1mmol Se-DPD and 3 ml of zinc precursor (1.5 g zinc stearate mixed with 6 ml ODE) reaction 20 min at 240 ℃. Then injection 1mmol DDT and 3 ml of zinc precursor and heated to 260 °C reaction 20 min. After purification, we could obtain InP/ZnSe/ZnS QDs. The purified InP/ZnSe/ZnS QDs and 5 ml OLA were added into three-necked bottle, the mixture was degassed to remove water, oxygen and hexane. Then the reaction was flooded with Ar and further heated to 250 °C. When the temperature reached 250 °C, 2.2 mmol S-TOP and 3 mmol of $Zn(OA)_2$ were injected immediately to coating another ZnS shell for 60 min then stop this reaction. The residual zinc stearate was reacted with S-TOP, which can increase the injection efficiency of holes. At the same time, the generated ZnS monomer can be coated on the surface of the QDs, increasing the thickness of the shell.

3 RESULTS

In this work, pure blue InP QDs were synthesized successfully by using $(DMA)_3P$, ZnI_2 and InI_3 as precursors, $(DMA)_3P$ is relatively stable when exposed in the air and does not generate toxic PH_3 gas compared with tris(trimethylsilyl)phosphine [$(TMS)_3P$], and its price is only one eightieth of $(TMS)_3P$. Since the lattice mismatch of ZnSe with InP is 3.3%, ZnSe can be used as the intermediate layer between the core InP and the shell ZnS to reduce the lattice mismatch. The FWHM of the resulting InP/ZnSe QDs was 47 nm and QY was 25%. After coating the ZnS layer, InP/ZnSe/ZnS QDs with

emission peak of 470 nm could be synthesized. The FWHM of the resulting InP/ZnSe/ZnS QDs was 47 nm and QY was 65%.

Confirmed by XRD and TEM, it is found that the excess zinc stearate added in the shell coating process prefers to coat on the QDs as clusters or grow into zinc stearate microspheres after the reaction (Fig. 1 and Fig. 2). In the aspect of device fabrication, to improve the carrier injection efficiency, the unreacted zinc stearate should be removed completely. The XRD shows that most of the microspheres can be removed by increasing the centrifugal speed (Fig. 2). The large size zinc stearate microspheres will precipitate and the XRD diffraction peak of zinc stearate gradually decreased as the increase of the centrifugal speed. However, it is difficult to completely remove the zinc stearate diffraction peak even at 11000 rpm when n-hexane and ethanol (or toluene) were used for purification (Fig. 1).

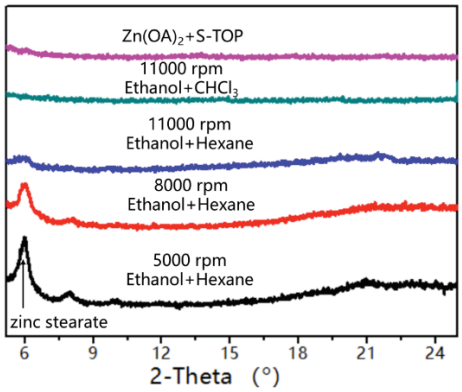

Fig. 1 Film XRD patterns of zinc stearate with different purification methods.

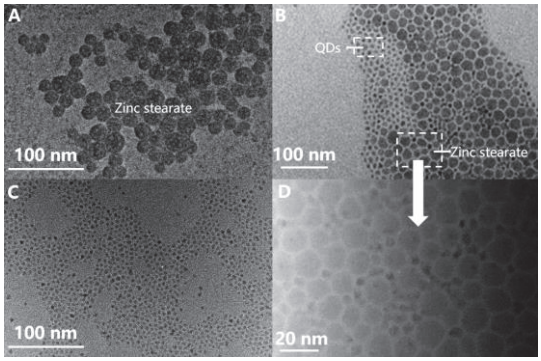

Fig.2 TEM of InP QDs with different purification methods. The speed of centrifuge is (A) 5000 rpm, (B) 8000 rpm, (C)11000 rpm, (D) Local magnification of 8000 rpm.

In order to completely remove zinc stearate, and meantime increase the shell thickness of QDs, we used S-TOP to react with zinc stearate. At the same time, the generated ZnS monomer could be coated on the surface of the QDs, which increases the thickness of the shell (Fig. 3). When the thickness of the shell increases, the stability of the QDs also improves obviously. The QY of the InP/ZnSe/ZnS/ZnS QDs shows a 51% decrease under the illumination at 365 nm Hg lamp with a power density of 8 mW/cm^2 irradiation for 10 hours compared to a 73% decrease of the InP/ZnSe/ZnS QDs. The main reason is that increasing the thickness of QDs can not only effectively isolate the external water and oxygen from the erosion of QDs, but also effectively confine electrons in the core to avoid being trapped by the surface defects.

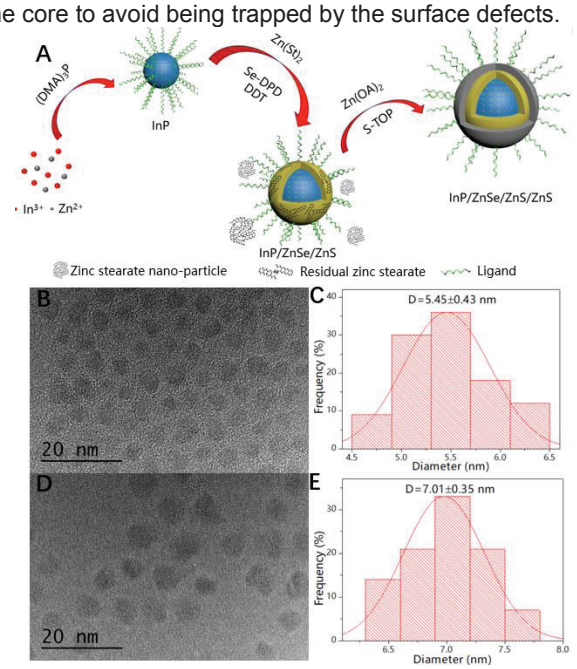

Fig. 3 (A) Schematic illustration for the synthesis of thick shell InP/ZnSe/ZnS/ZnS QDs. (B) TEM image and (C) Histogram of size distribution of InP/ZnSe/ZnS QDs. (D) TEM image and (E) Histogram of size distribution of InP/ZnSe/ZnS/ZnS QDs.

4 DISCUSSION

To verify the positive effects of QDs optimization methods on devices, we fabricated QLED with the device structure of indium tin oxide (ITO)/ PEDOT:PSS/ PVK/ QDs/ $Zn_xMg_{1-x}O$ NPs/ Al.

The maximum current efficiency (CE) of the InP/ZnSe/ZnS/ZnS QLED is 3.6 cd/A, which is nearly three times as high as that of InP/ZnSe/ZnS QLED (1.3 cd/A, Fig. 4C). The maximum EQE also increased by three times (Fig. 4D), i.e. from 0.6% to 1.7% measured from 14 devices. The luminance of InP QLED increases from 25 cd/m^2 to 140 cd/m^2 at 6V (Fig. 4E). The current density also is improved from 32 mA/cm^2 to 125 mA/cm^2 at 8 V (Fig. 4F). At the same time, due to the improved carrier injection efficiency, the turn-on voltage drops from the original 4.2 eV to 3.1 eV. The improvement of device performance is mainly due to two factors. Firstly, the increase of the shell thickness of QDs can reduce the energy transfer in the QLED. Secondly, the residual zinc stearate is reacted with S-TOP, which reduces the barrier of hole injection (Fig. 5).

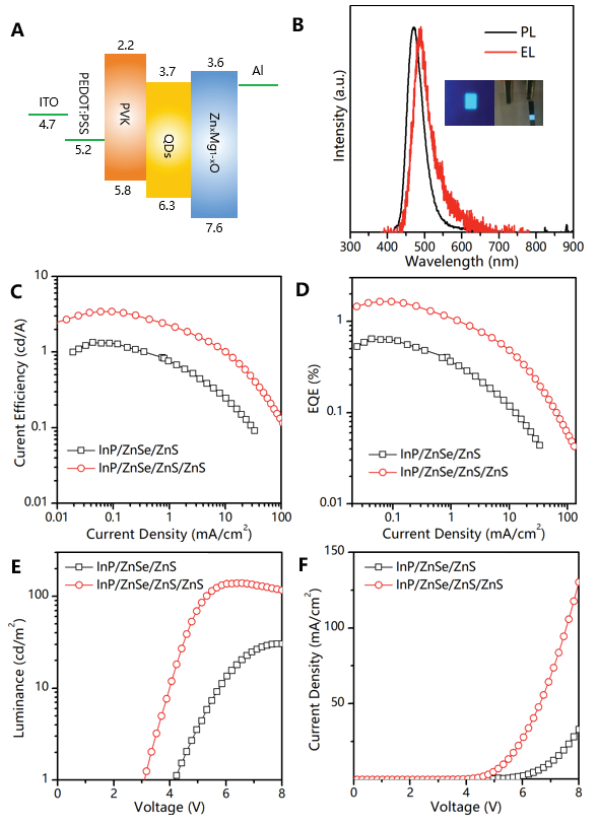

Fig. 4 (A) Energy level diagram for QLED devices. (B) PL and EL spectral of InP/ZnS/ZnS QDs. Device characteristic of InP/ZnS and InP/ZnS/ZnS QLED (C) Current efficiency versus current density. (D) EQE versus current density. (E) Current density versus voltage. (F) Luminance versus voltage.

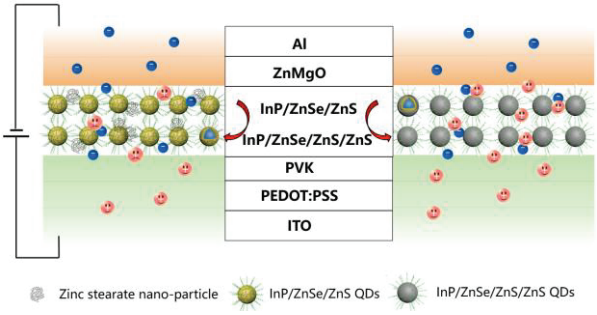

Fig. 5 Schematic illustration for the comparison of InP/ZnSe/ZnS QLED and InP/ZnSe/ZnS/ZnS QLED carrier injection efficiency.

5 CONCLUSIONS

In summary, we successfully synthesized thick-shell blue-light InP/ZnSe/ZnS/ZnS QDs using the cost effective and less toxic $(DMA)_3P$ as the precursor of phosphorus. The QY of blue QD can reach up to 65%. By adding excessive S-TOP to react with unreacted zinc stearate, as a result, the residual zinc stearate could be completely reacted, enhancing the injection efficiency of holes. At the same time, the generated ZnS monomer can be coated on the surface of the QDs, increasing the thickness of the shell, and reducing the energy transfer between QDs. EQE can reach 1.7% for the blue-light InP QLED.

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